AN ANALYSIS OF COMPOSITIONAL AND MICROSTRUCTURAL EFFECTS ON THE RESISTANCE OF A PROTOTYPE SPARK PLUG RESISTOR MATERIAL

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AN ANALYSIS OF COMPOSITIONAL AND MICROSTRUCTURAL EFFECTS ON THE RESISTANCE OF A PROTOTYPE SPARK PLUG RESISTOR MATERIAL

Approved:

Alan T. Chapman, Chairman

Joseph L. Pentecost

Joe K. Cochran, Jr.

Date approved by Chairman: June 2, 1978

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SUMMARY

This investigation considered the compositional parameters of a spark plug resistor mix where the principle components were a borosilicate glass, titania powder, boron carbide particles, and a silicone resin binder. Further, a model was devised to explain the conduction of the current through the resistor mix. This was accomplished using compositional information in conjunction with a detailed microstructural analysis of the resistor mix.

The microstructural analysis revealed that the sealed resistor mix had a laminar structure that was perpendicular to the electrodes between the electrodes and parallel to the electrodes along the bore wall of the insulator. The TiO_2 particles spread out in the layers between the glass particles and was the primary conductor in the resistor mix. The B_4C particles served as conduction paths connecting some layers of TiO_2. The binder content affected the resistance values because it reduced the TiO_2. The anisotropy of the resistor macrostructure effectively served to minimize variable resistance values caused by non-uniform dimensions of the various components of the spark plugs.

CHAPTER I

INTRODUCTION

Ceramic resistors have been incorporated with spark plugs since the advent of automobile radios. The discharge of high voltages across the spark plug gap generates radio frequency interference. One method of reducing the interference is to place a ceramic resistor in the bore of the spark plug insulator in series between the electrodes. There is little, if any, information in the non-patent literature on a high temperature ceramic resistor for spark plug application.

There are many characteristics which a resistor spark plug should possess. The two primary characteristics are that the resistance value of the spark plug be sufficient to suppress the interference, and that the resistance value be maintained under engine operating conditions and during repeated usage over long periods of time. These conditions necessitate the use of ceramic materials because conventional electric resistor materials fail at high temperatures and high voltages. A resistor composition is typically glass and semiconductors mixed with a binder. The resistor mix is placed in the bore of the spark plug insulator between the electrodes and the assembly is heat treated to seal the resistor mix and the electrodes in the insulator.

Many parameters affect the final resistance value created by a resistor mix in a spark plug. The purpose of this investigation was to study the compositional parameters of a resistor mix where the principle components were a borosilicate glass, titania powder, boron carbide particles, and a silicone resin binder. The selection of these components was based on a prototype composition and on evaluating many compositions reported in the patent literature, and the effects of each component on the spark plug resistance were studied. A second objective of the investigation was to devise a model which explained the conduction of the current through the resistor mix. This was accomplished using the compositional information in conjunction with a detailed microstructural analysis of the sealed resistor mix. It is hoped that the results of this investigation will advance the understanding of ceramic resistors for spark plug application and solve some of the problems associated with the production of resistor spark plugs.

CHAPTER II

SURVEY OF LITERATURE

This literature survey is a review of the state of the art of ceramic resistors as incorporated in spark plugs. A brief introduction is given on the purpose and design of resistor spark plugs, and the composition and desirable characteristics of the resistor mix. Most of the information on the state of the art is contained in patents, and therefore details are limited. The pertinent characteristics are discussed of each resistor mix component studied in this research.

Purpose and Design of Resistor Spark Plugs

The purpose of the resistor spark plug is to damp out radio frequency oscillations which occur when the spark discharges. The oscillations cause automobile radio frequency interference particularly in AM and shortwave reception, and they cause rapid erosion of spark plug electrodes.[1,2] They also may interfere with other electronic equipment in close proximity to the automobile.[3] Burgett, et. al.[4] explains that a spark plug acts as a capacitor which discharges when the spark occurs, generating interference. A resistor spark plug suppresses the interference by dividing the capacitive effect and reducing the radio frequency interference. The voltage discharge oscillations of resistor and non-resistor spark plugs are compared in Figure 1.

In the bore of a spark plug, the lower electrode where the spark occurs is called the center wire and the upper electrode is called the terminal screw, as shown in Figure 2. Standard spark plugs have the two electrodes connected and sealed in place by an electrically conducting metal-glass seal.[6] Resistor spark plugs differ in that the glassy seal incorporates a ceramic resistor mix.

Most ceramic resistor mixes do not bond well to the electrodes, but they do bond well to metal-glass seals similar to those used in standard spark plugs.[1] In addition, some of the components that may be used in the resistor mix are organic and subject to oxidation at spark plug operating temperatures.[3] For these two reasons, the resistor mix is often positioned between two layers of a metal-glass composition, as shown in Figure 3. The metal-glass composition, typically copper-glass, serves as a seal to protect the resistor mix from oxidation and it bonds well to the resistor mix, the insulator and both electrodes. This layering process is called three-step loading. If adequate bonding can be achieved between the resistor mix and the electrodes, one or both copper-glass seals may be eliminated in which case the resistor mix also serves as the sealing and bonding mechanism.

In assembling the resistor spark plug, the center wire is placed in the insulator and is usually supported by a

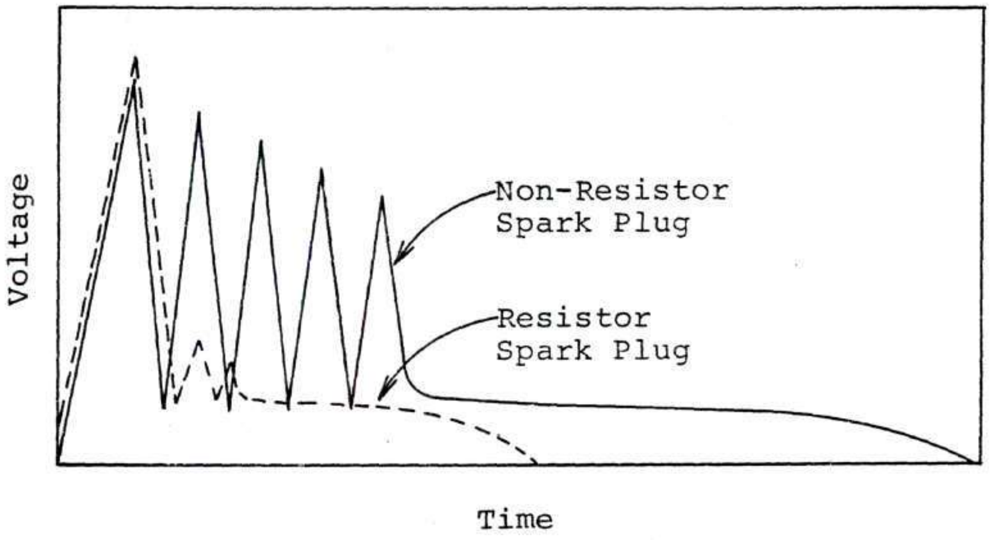


Figure 1. A Comparison of the Voltage Oscillations of Resistor and Non-Resistor Spark Plugs[5].

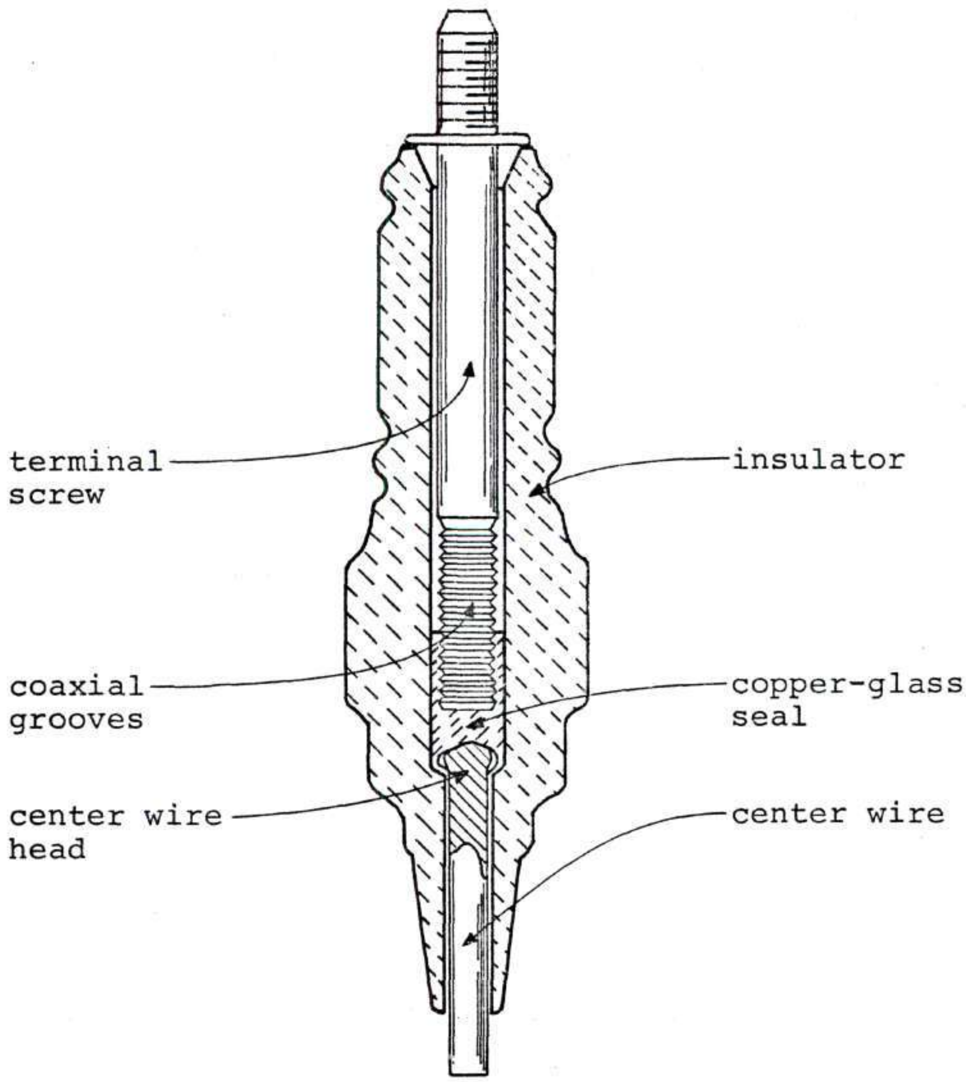


Figure 2. A Schematic Drawing Displaying the Internal Parts of a Non-Resistor Spark Plug.

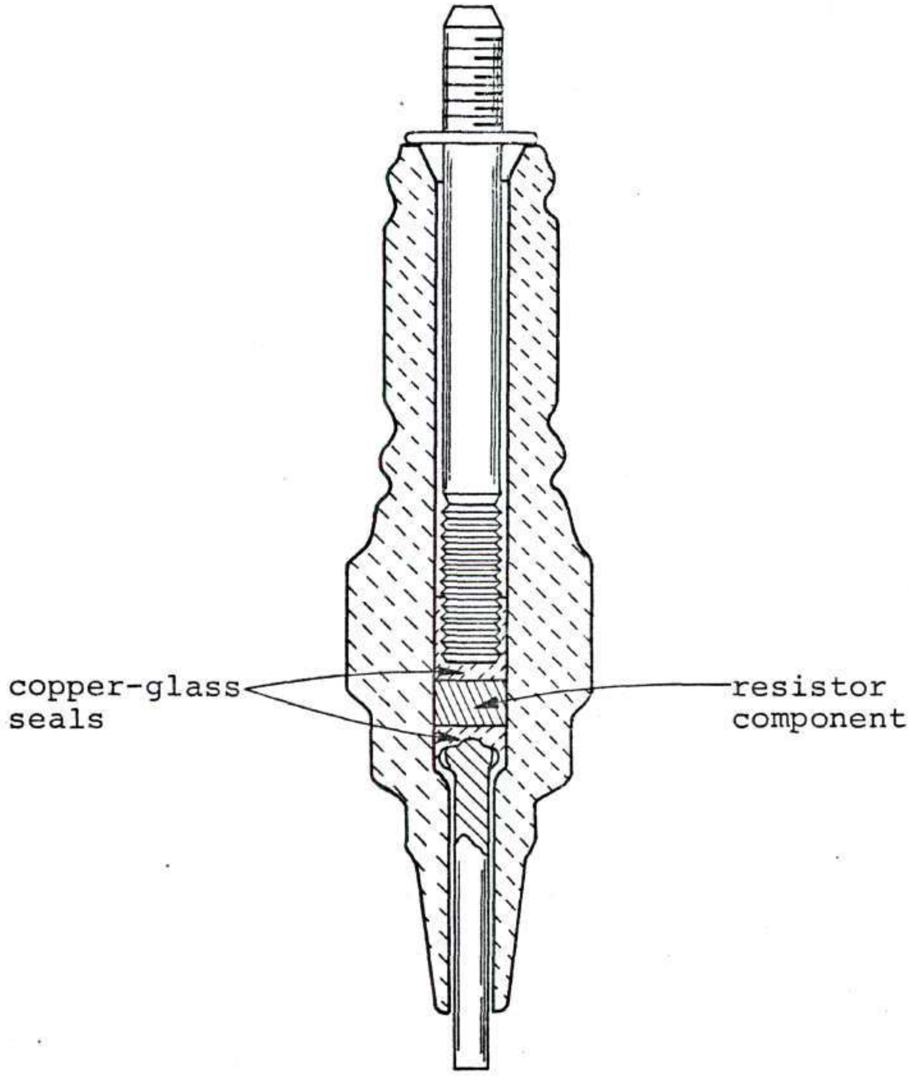


Figure 3. A Schematic Drawing Showing the Resistor Component and Copper-Glass Seals of a Resistor Spark Plug.

shoulder in the bore. A lower metal-glass powder, the resistor mix, and an upper metal-glass powder are placed in the bore on top of the center wire. These components are pre-pressed, either individually or as a group, to increase the density of the final, sealed resistor mix. The terminal screw is positioned on top, protruding above what is to be its final position. This assembly is fired to a temperature sufficient to soften all the glass and the terminal screw is hot-pressed into the bore. The pressure causes the molten, conductive metal-glass to fill all space around the head of the center wire and the lower end of the terminal screw. The resistor mix remains between the metal-glass seals. The assembly is allowed to cool under pressure until all components are firmly bonded in place. The result is a spark plug as shown in Figure 3 with electrodes tightly sealed to the insulator and to the resistor mix by the metal-glass seals. In the cases where one or both metal-glass seals are not required, a similar procedure is used without the unneeded seal(s).

The resistor mix is basically a glass containing semiconductor materials. There may also be inert fillers, metal powders, carbonates, other carbonaceous materials, reducing agents, and/or a binder. These components, when mixed thoroughly and sealed by heating in the bore of the spark plug, create a dense, low porosity mass. The result is a series of semiconductor particles separated by glass and other non-conducting components. The ignition current jumps from particle to particle as it moves through the resistor mix. The spark plug resistance value is primarily dependent on the characteristics and amounts of the components in the resistor mix, but other factors including sealing temperature and furnace atmosphere also affect the resistance values.

The manufactured resistor spark plug must have a given resistance value, usually around 10 kΩ, and low scatter of the resistance values is desirable. In operation, the sealed resistor mix, which serves as all or part of the seal between the electrodes, has to be strong to prevent the electrodes from becoming loose, and impervious to engine cylinder gases under pressure. The resistance value should have low temperature and voltage coefficients, and it should exhibit little electrical aging (change in electrical properties with time, particularly due to applied voltage). All these characteristics must be maintained up to 540°C.[7]

Review of the Patent Literature

There are three broad categories of resistor mixes for use in spark plugs. One category uses a semiconductor, such as titanium dioxide, and one or more reducing agents. Another category includes the use of a carbonaceous material, a reducing agent, and a metallic carbonate. The final category uses a ceramic filler and a tin oxide resistor component.

In all cases a glass is used as a structure to hold the other components.

A patent representative of the first category was granted to Heischman[3] in 1963. It discloses a resistor mix consisting of a borosilicate glass, titanium dioxide and boron carbide, all held together with a binder. Corning glass #7070 is used because it has a low thermal expansion of 3.2×10^{-6} inches/inch/°C. Titanium dioxide, pigment grade, is easily reduceable to form suboxides which are semiconductors. Boron carbide, 220 mesh, acts as a semiconductor and a reducing agent. The binder is Methocell, 8000 cps., a water soluble cellulose gum, which also acts as a reducing agent.

An important factor in Heischman's patent is that the need for metal-glass seals on either side of the resistor mix is eliminated. There are two reasons for this. The components used are inorganic and are, therefore, relatively stable at the operating temperatures and pressures of spark plugs. So, they do not need protection from oxidation.

Also, the electrodes are designed in a manner that promotes bonding with the glassy resistor mix. The terminal screw is threaded at its lower end. It also has a thermal expansion greater than that of the resistor mix, due to the low thermal expansion of the glass. The terminal screw cools after hot-pressing and contracts more than the resistor mix. Tension is created between the terminal screw head on top and the lower terminal screw grooves which are mechanically seated in the resistor mix.

The center wire has a thermal expansion of 13×10^{-6} inches/inch/°C and the head is shaped cylindrically, with upper and lower flanges curved inwardly. This design creates circular concave lips which, upon cooling, firmly secure the resistor mix to the center wire. The center wire head also has a raised middle area for more electrical contact with the resistor mix, and there are vertical ridges on the outer part of the center wire head to prevent turning. The designs of these electrodes result in good mechanical seals which allow ample contact with the resistor mix, eliminating the need for intermediate metal-glass seals.

An example of a composition from this patent (in weight percent) is 88.0 w/o Corning #7070 glass, 9.5 w/o TiO_2, 2.0 w/o B_4C and 0.5 w/o Methocel. This gives a resistance value of 10 kΩ. In all compositions, the amounts of Methocel and B_4C are held constant. The resistance value is controlled by adjusting the TiO_2/glass ratio, which is inversely proportional to the resistance value.

For production, water is added to the mixed components, the mix is dried, granulated, and loaded into the spark plug, and the assembly is heated to 900°C. The terminal screw is pressed in and the assembly is allowed to cool to below red heat, at which time the pressure is removed.

Heischman notes factors, other than the composition, which affect the resistance value and the seal. These include the dimensions of the resistor mix after sealing, the furnace atmosphere, whether reducing or oxidizing, and the sealing temperature.

The patent granted to Webb, et. al., in 1971 is typical of the second category of resistor mixes,[1] and improves on two earlier patents.[8,9] This patent claims to satisfy the desired requirements of resistor spark plugs with an extensive and complicated composition. The glass is a barium borate, the amount of which has little effect on the resistance values. An inert filler such as kyanite, zirconia, or mullite, etc., controls the fluidity of the mix during hot pressing. Bentonite is used as the binder to get the mix into granular form for volumetric loading. Organic binders are not used because they cause the resistance values to be unstable. Carbon black is added as a reducing agent or a conducting medium. A water soluble, carbonaceous material such as sucrose, Methocel, or corn flour, etc., is used to combine with the carbon black and/or semiconductor material to reduce the electrical aging of the resistor mix.

The Webb, et. al., patent reveals the use of certain metallic carbonates and metal powders which reduce the porosity of the resistor mass and strengthen the bond between the resistor mass and the center wire, thereby elminating the need for a lower metal-glass seal. The carbonates are of lithium, zinc, sodium, or magnesium and the metal powders are zinc, antimony or tellurium. The melting points of these range from 300 to 820°C; at a sealing temperature of 870 to 930°C, these materials are probably in a liquid form during hot pressing. The carbonate decomposes and gives off carbon dioxide. The cation enters the glass phase and modifies the viscosity of the glass in order to inhibit the flow of the molten metal powder below the center wire head. This patent claims that the molten metal coats the center wire head forming a strong bond between the center wire head and the glassy phase of the resistor mix. This bond eliminates the need for a lower metal-glass seal, but an upper seal is still needed. The modified glass is also less porous, thereby strengthening the resistor mix.

Included in this patent is also the use of a semiconductor material for cases of extreme electrical requirements, as described by Counts, et. al.[7,9] In one case,[9] the material is a binary metal oxide system, particularly sintered titanium zirconate. Before incorporating the semiconductor material in the resistor mix, the material is heated in the range of 1260°C to 1620°C for one to 24 hours, and cooled and ground to -200 mesh. In the other case,[7] the material is a stannous titanate semiconductor and must be pre-reacted similar to the above procedure. In both cases, the resistance value is controlled by the content of the semiconductor material and by the carbon black, which is used to reduce the semiconductor material.

An example of a resistor mix (in parts by weight, pbw) consists of 0.5 pbw lithium carbonate, 5 pbw zinc, 30 pbw barium borate glass, 44 pbw zirconia, 25 pbw Indian Kyanite, 1.8 pbw Thermax (carbon black), 0.34 pbw sucrose and 1.83 pbw bentonite. The resistor mix size is -28, +100 mesh and it is volumetrically loaded into the insulator. The sealing temperature is 915°C with an 18 minute heating period followed by a 7 minute hold at 915°C.

A patent granted to Yoshida and Sakai,[10] from Japan, in 1977 is similar to the Webb, et. al., patent, making use of metals and carbonaceous materials for sealing, strength and electrical stability. An important difference is the Japanese use no carbon black, stating that it causes unevenness in the resistance values. A carbonaceous material is the sole source of carbon.

The third type of resistor mix is described in the patent granted in 1977 to Oki, et. al.[2] A theory is proposed where the radio frequency noise can be suppressed if the electric current moving through the spark plug can be made to "zigzag." This is accomplished with a resistor mix containing three basic materials, a resistor component, a ceramic filler, and a soft glass.

The resistor component and ceramic filler work together to create the zigzag path. The resistor component is primarily tin oxide, with small additions of carbon powder, antimony oxide, tantalum oxide, aluminum phosphate and/or a binder. The resistivity of tin oxide produces spark plug resistance values from several kΩ to several tens of kΩ. The ceramic filler such as alumina, zirconia, and quartz glass, etc. has a resistivity much higher than the resistor component. Since the current does not flow through the filler but flows through the resistor component, current "zigzags" through the resistor mix.

The third component, a soft glass, may be of almost any composition with a softening temperature between 300 and 600°C. The softening temperature is above 300°C because engine operating temperatures are up to about 250°C. This value is low compared to other resistor mixes which are designed to operate up to 540°C.[7] This patent proposes that spark plugs with glasses that have softening temperatures above 600°C give high noise levels when tested in automobiles. This is because the glasses are not fluid enough during the hot pressing to permit the resistor mix to bond well to the bore of the insulator and to the copper-glass seals. In contrast to Webb, et al., Oki, et al., says the amount of glass does affect the resistance values, but that the stability of the resistivity of tin oxide considerably reduces this effect.

A satisfactory composition (in volume percent) contains 10 v/o glass, 70 v/o filler and 20 v/o resistor component. There is no binder; the three components are just mixed in a ball mill. The composition of the glass (in weight percent) is 11 w/o B_2O_3, 11 w/o Al_2O_3, 3 w/o SiO_2, and 75 w/o PbO. It has a thermal expansion of $8.3 \times 10^{-6}/°C$ and a softening temperature of 440°C. The filler is quartz glass which has a softening temperature of 1650°C. The resistor component contains 87 w/o SnO_2, 10 w/o Ta_2O_5 and 3 w/o Sb_2O_3, which are calcined together at 1200°C before being mixed with the glass and filler. This composition gives a spark plug resistance value of about 5 kΩ. The resistance value is adjusted by changing the amount of tin oxide in the resistor component. The amounts of the other components, including the total amount of the resistor component, remain constant.

Copper-glass seals are used on both sides of the resistor mix. The copper-glass powders and the resistor mix are loaded by weight and each is pressed into the bore with about 50 kg/cm^2 as it is loaded. The assembly is heated in an electric furnace at 850°C for 30 minutes. It is removed from the furnace and the terminal screw is pressed with 50 kg/cm^2.

Properties of Resistor Mix Components

The selection of the components of the resistor mix studied in this research was based on a prototype composition and on the first category of resistor mix described above The materials are titanium dioxide (anatase structure), boron carbide, a borosilicate glass and a silicone resin binder. A discussion follows of the applicable characteristics and properties of these materials. The specifications of the particular products that were used are given later.

Electrical Characteristics of TiO_2

Titanium dioxide is a semiconductor with two structures, anatase and rutile, which are stable at room temperature. When anatase is heated to between 800 and 1100°C, it changes to rutile,[11] which structure remains when the sample is cooled to room temperature. The intrinsic resistivity of rutile[12] is about 10^{13} Ω-cm at room temperature, 10^{2} Ω-cm at 300°C, and 10^{-3} Ω-cm at 1000°C. Other values are reported[13-16] and the discrepancies are probably due to specimen preparation measurement techniques, or the oxidation condition.

The resistivity of rutile changes as a function of stiochiometry because rutile is a reduction type semiconductor which readily forms suboxides of TiO_{2-x}. The extent of the oxygen loss strongly depends on the temperature and the atmosphere in which the TiO_2 is treated. Table 1 presents data for the effect of heat treatment on the electrical resistivity of samples that were pressed and then fired in nitrogen. Table 2 shows the effects of atmosphere and temperature for sintered samples of TiO_2 (rutile). The effect of hydrogen reduction on rutile ceramics is shown in Figure 4. This figure is presented not only to show the effects of temperature but also that the reduction time has little effect, at least at 800°C. Further, the resistivities of the samples changes less than one order of magnitude when the temperature at which the resistivity is measured is varied from -170°C to 727°C. The slope is positive between 20°C and

Table 1. The Electrical Resistivity at Room Temperature and the Temperature Coefficient of Resistivity of TiO_2 Samples Fired in Nitrogen.[17]

Heat Treatment (°C)	Resistivity (Ω-cm)	Temp. Coeff. of Resistivity (20-200°C)
950	4.34×10^5	$+1.2 \times 10^2$
1000	1.42×10^6	$+3.1 \times 10^2$
1200	1.9×10^7	$+4.2 \times 10^1$

Table 2. The Electrical Resistivity (Ω-cm) of Rutile as a Function of Sintering Atmosphere and Temperature.[18]

Sintering Atmosphere	Sintering Temperature 1300°C	Sintering Temperature 1400°C
N_2	6.4×10^5	6.0×10^3
Air	10^{11}	1.4×10^6
O_2	10^{11}	10^{12}

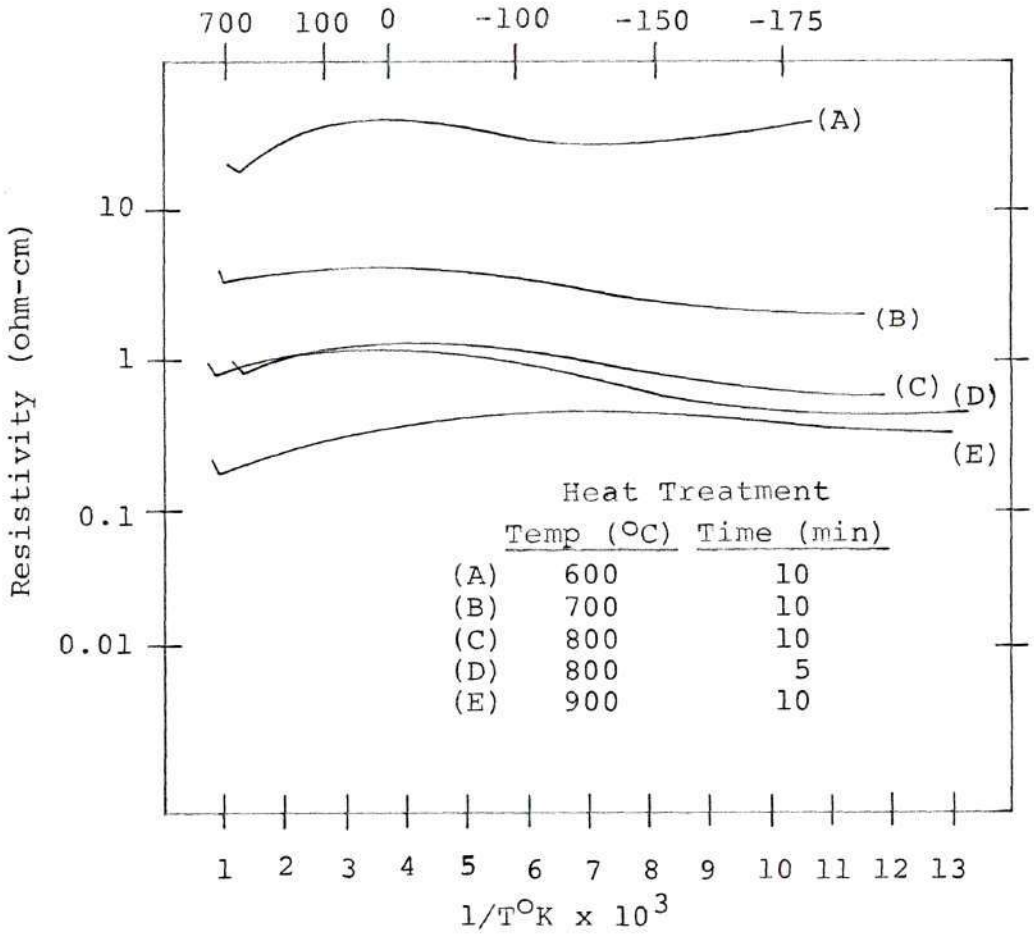


Figure 4. Electrical Resistivities of Samples of TiO_2 (Rutile) Heat Treated and Reduced in Hydrogen[18b].

200°C indicating a negative temperature coefficient of resistivity in that range, as opposed to the positive coefficients for non-reduced samples presented in Table 1. Figure 5 shows the effect of oxygen pressure on resistivity.

The maximum value of x in TiO_{2-x} has been debated. When reducing TiO_2, but maintaining the rutile structure, it may be as high as 0.01, but x can be much larger when specific crystals are flux grown.[19,20] Tables 3 and 4 are presented to give a quantitative idea of the change in resistivity as a function of stoichiometry. Table 3 was developed from information on samples heated to high temperatures at various oxygen pressures to form non-stoichiometric rutile. Table 4 comes from information on flux grown single crystals of titanium oxides tested at room temperature.

The quantitative effect of titania in a resistor mix sealed in a spark plug is difficult to determine. The information in Tables 2, 3, and 4 and Figure 5 is on single crystals or polycrystalline pellets whose density approaches that of the theoretical value. Neither condition is realized in a sealed resistor mix. The resistivity depends not only on the inherent properties on the suboxide created by heating, but also on the shape, orientation and packing of the polycrystalline conglomerates.[14]

Qualitatively, under spark plug sealing conditions, the extent of the reduction of the titania probably falls in the area of the information in Table 3. Even a slight reduc-

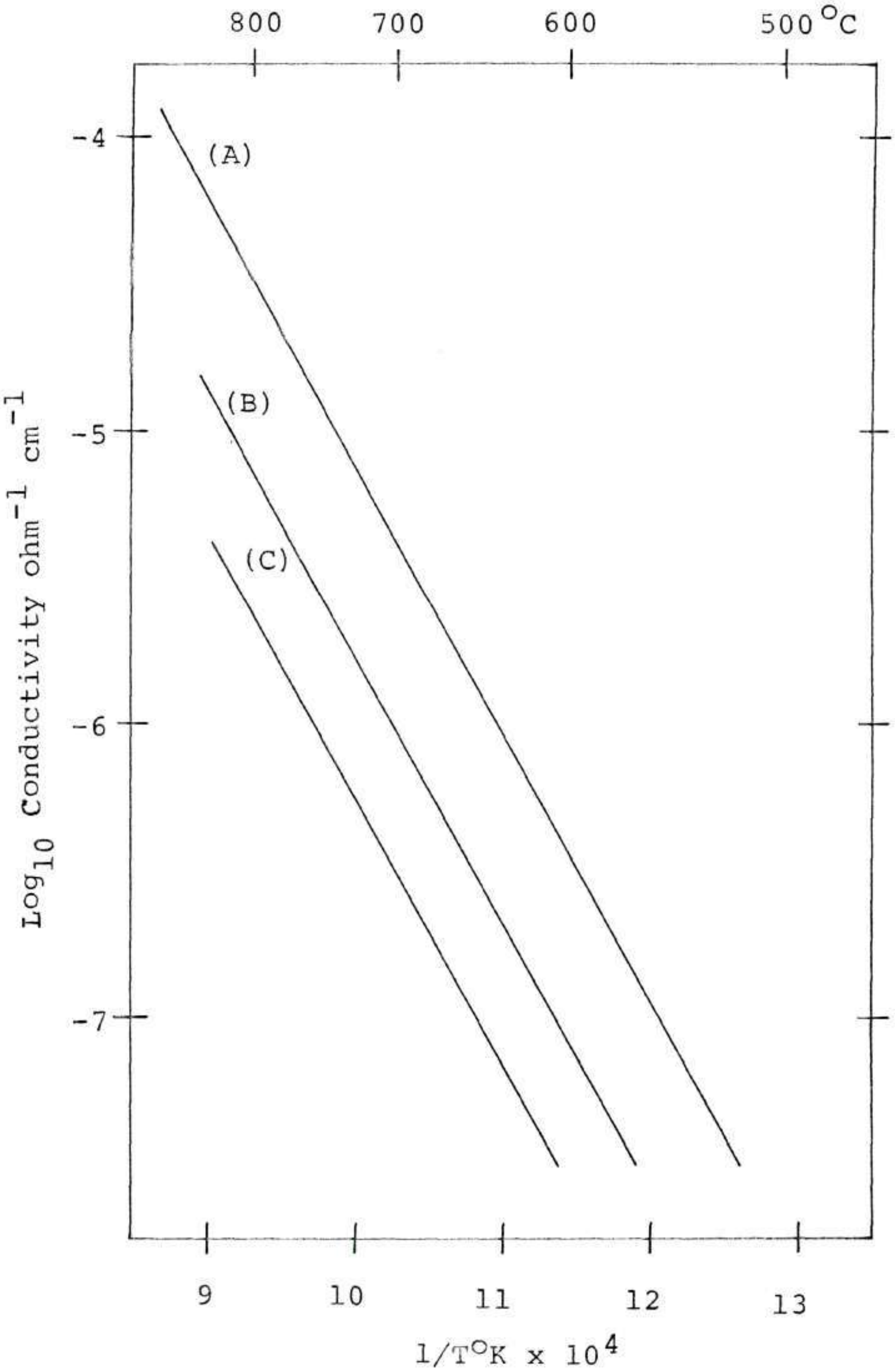


Figure 5. Electrical Resistivities of Unsintered Samples of TiO_2 (Rutile) at Oxygen Pressures of (A) 1.3×10^{-4} atm., (B) 6.6×10^{-2} atm., and (C) 1.05 atm.[16].

Table 3. The Resistivity as a Function of Small Values of X in TiO_{2-x} for Rutile Samples Heated to 1000°C at Various Oxygen Pressures.[19]

$X(x10^{-4})$ in TiO_{2-x}	P_{O_2} (atm)	Resistivity (Ω-cm)
1	10^{-8}	14
2	10^{-10}	5.0
7	10^{-12}	1.7
10	10^{-14}	0.50

Table 4. The Resistivity of Flux Grown Titania Oxides as a Function of Large Values of X in TiO_{2-x} at 27°C.[20]

X in TiO_{2-x}	Resistivity (Ω-cm)
0.125	3.2×10^{-2}
0.167	1.3×10^{-2}
0.200	1.9×10^{-3}
0.250	6.3×10^{-4}
0.333	7.1×10^{-1}

tion of TiO_2 greatly decreases the resistivity from the stoichiometric, room temperature value of 10^{13} Ω-cm.

Titanium dioxide experiences electrical aging when an electric field is applied. During this process one observes evolution of oxygen from the specimen[20b] which seemingly reduces the resistivity. An increase in the oxygen vacancy concentration causes a change in the resistivity as a function of temperature. The electrical aging of titania is at least one of the causes of the reduction of the spark plug resistance values during use in an automobile engine.

Properties of Boron Carbide

Boron carbide is a semiconductor that exhibits the expected negative temperature coefficient of electrical resistivity. The literature contains many temperature-resistivity studies of boron carbide.[21-24] Various results have been reported and the results of Golikova, et.al., are given in Figure 6.

Most of the literature reports that B_4C does not oxidize below 600°C, although Litz and Mercuir[25] report slight oxidation as low as 450°C. Nazarchuk and Mekhanoshiva,[26] using B_4C in the size range of 62 to 74µm, report that the oxidation increases at 700°C, it levels off between 800-1000°C, and it increases sharply at 1200°C. They say the leveling off range is due to the formation of B_2O_3, which protects the B_4C from attack by oxygen. The B_2O_3 volatilizes rapidly at 1200°C and the oxidation of the B_4C

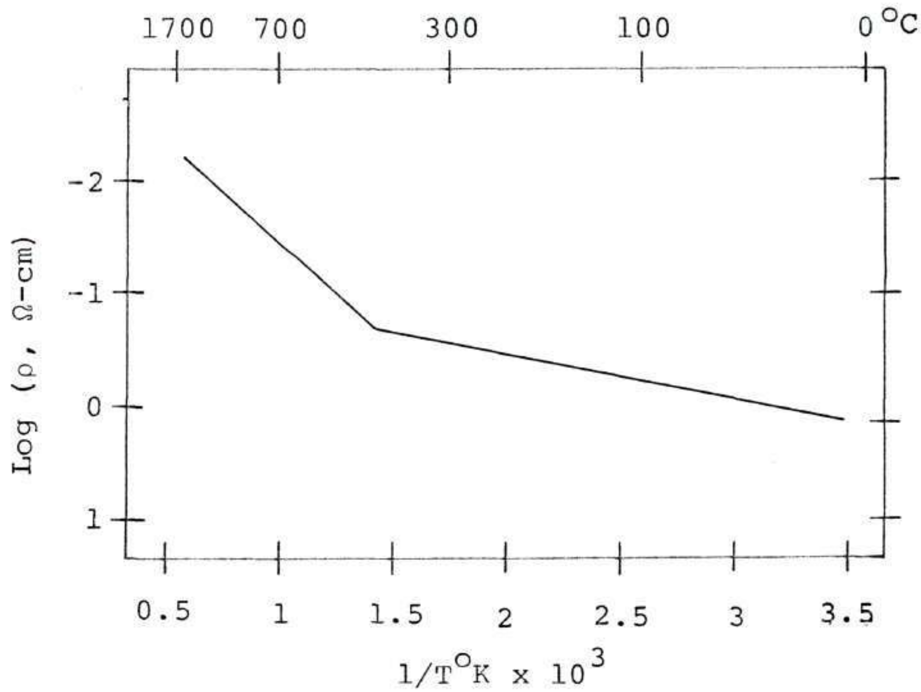


Figure 6. The Electrical Resistivity of Boron Carbide[21].

continues. They also claim that B_4C invariably contains a minimal amount of carbon which reduces the oxidation resistance of the B_4C.

Nazarchuk and Mekhanoshiva further report that coarse powders of B_4C form an outer vitreous layer at 800°C in oxygen and do not burn up, whereas fine powders oxidize as freely as carbon. Litz and Mercuri use B_4C in the size range of 75 to 106μm and report that after their experiments the B_4C particles were covered with vitreous B_2O_3. Dominey[27] concludes that a B_2O_3 film reduces the oxidization rate. He also says that decreasing the particle size and the inherent splitting of the B_4C particles due to oxidization increase the oxidization rate.

Properties of Borosilicate Glasses

Borosilicate glasses have a high electrical resistivity relative to soda silicates and the temperature coefficient of electrical resistivity is negative.[28] Westhuizen, et al.,[29] has shown that remelting Pyrex (13 w/o B_2O_3) does not significantly alter the resistivity. But Dgebuadze and Mazurin[30] report that the resistivity of soda silicates with 26 w/o and 37 w/o B_2O_3 increases, respectively, 2.2 and 0.7 orders of magnitude after heat treatment.

Borosilicates are resistant to both heat and chemical attack. When heated at 1200°C for one hour, the volatilization, measured by weight loss, is less than 0.1 weight percent according to Oldfield and Wright.[31] Heslop[32] reports that at 150°C there is negligible attack by most acids and alkalines, hydrocarbons, and oxidizing or reducing chemicals.

Wilson and Carter[33] have shown that the diffusion coefficient of sodium in Pyrex is less than that in a soda-lime glass. High melting point materials can be heated with a borosilicate glass to its softening point and, after cooling, the glass will serve as a rigid structure to hold or bond together the materials.

Binder Effects

A binder facilitates the handling of powdered materials. When a silicone resin binder is heat treated at a sufficient temperature and time, it is completely transformed to silica which must then be considered in the composition. As the methyl group is burned off, it combines with oxygen that is both in the air and in any other components present which are subject to reduction.

CHAPTER III

MATERIALS, PROCEDURES AND EQUIPMENT

This chapter describes the specific materials used in developing the trial resistor mixes. The materials were titanium dioxide, boron carbide, a borosilicate glass and a silicone resin binder. A description is given of all procedures and equipment for handling the materials, formulating the trial resistor mixes, sealing the mixes in spark plugs, measuring the spark plug resistance values, and sectioning the spark plug for microstructural examination.

Components of the Resistor Mix

The titania had the anatase structure and was a Baker Analyzed Reagent, (lot no. 38356). It was passed through a 100 mesh screen to break down conglomerates in order to promote uniform mixing. The boron carbide was produced by Cerac (IPB-25-13047-64; stock no. 1285), with 7.5 w/o between -270 and +325 mesh, and the balance -325 mesh. The binder was Dow Corning Release Coating, a silicone resin binder originally developed for use in bakery bread pans. The low viscosity of this binder gave it good wetting characteristics. The composition is proprietary but the binder oxidizes to silica when heat treated in air. Further heat treating information is given in Appendix A.

The borosilicate glass was Corning 7070 and is described by Hutchins and Harrington.[34] Corning 7070 is a low loss electrical type glass with the following composition (w/o): 71 SiO_2, 26 B_2O_3, 1 Al_2O_3, 1 K_2O, 0.5 Li_2O, and 0.5 Na_2O. The thermal expansion from 0°C to 300°C is 3.2×10^{-6}/°C, and from room temperature to 460°C it is 3.9 $\times 10^{-6}$°C. The strain point is 455°C at a viscosity of $10^{14.5}$ cps. Figure 7 shows the volume resistivity as a function of temperature. Three specific values of the $\log_{10}$ volume resistivity (Ω-cm) given by Hutchins and Harrington at 25, 250, and 350°C are, respectively, 17+ (estimated), 11.2 and 9.1.

Mixing the Components and Loading the Insulators

The TiO_2 and the B_4C were weighed using an Ainsworth analytical balance and the measurements were accurate to $\pm$0.01 g. The glass and the binder were weighed using an Ohaus triple beam balance and the measurements were accurate to $\pm$0.5 g. In each series of trial resistor mixes, the effect on the spark plug resistance values of the amount of one component was studied. A large amount of the other components (except the binder) was mixed and then divided into equal amounts. The component being studied, either the TiO_2, B_4C or binder, was added in the various amounts. In all cases the binder was added last. Each trial resistor mix weighed 25 to 30 g total.

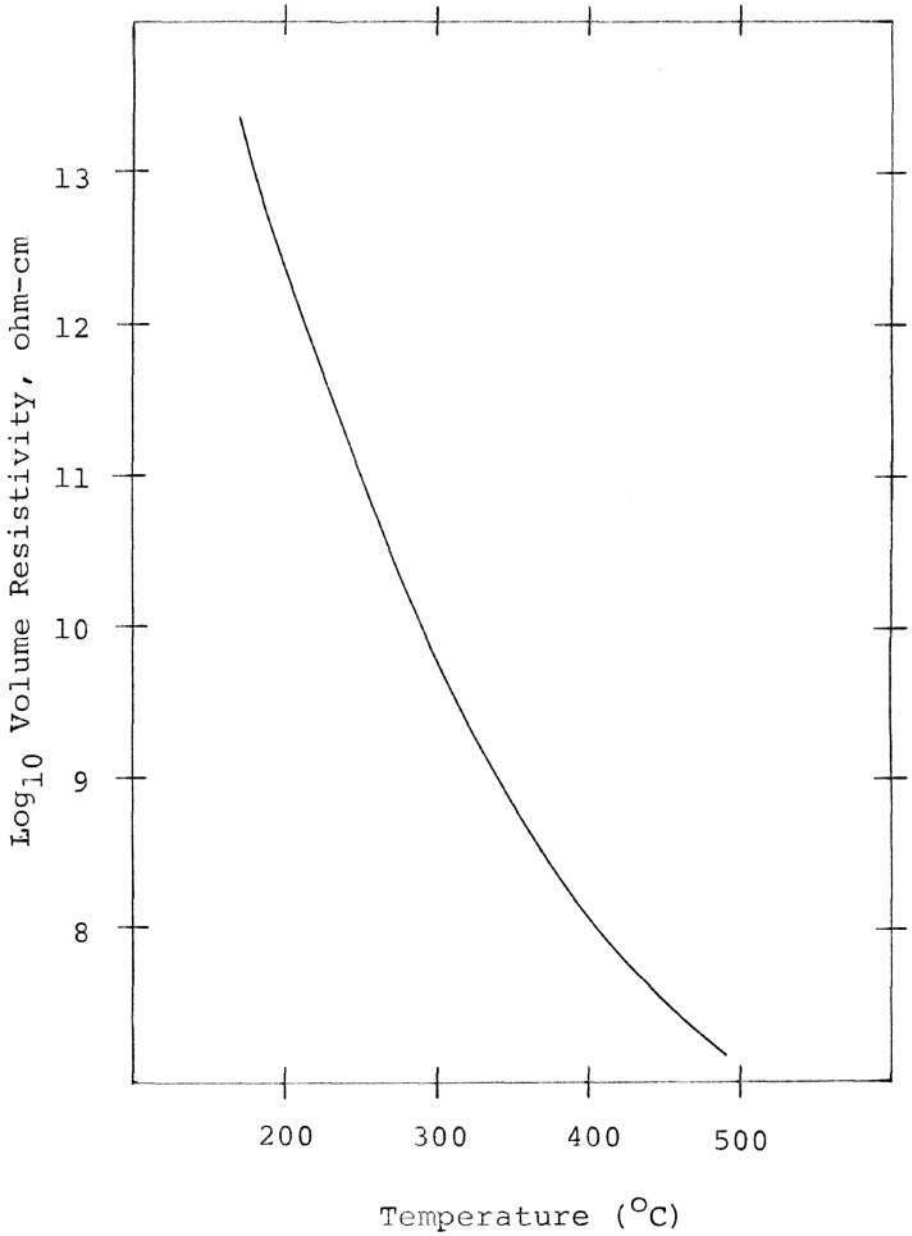


Figure 7. The Volume Resistivity of Corning 7070 Glass[34].

The dry components were mixed by hand until the TiO_2 and B_4C appeared well dispersed in the glass. The binder was added and hand mixing was continued for about five minutes until the binder was absorbed by the material and wetting appeared uniform. The mixes were dried in air and carefully granulated with a mortar and pestle. They were finally screened to yield 95 w/o of -28, +100 mesh and 5 w/o of -100 mesh.

Spark plug insulators, terminal screws, center wires and a copper glass were obtained from a spark plug manufacturer. Descriptions of these are given in Appendix B. The copper glass was a layer on top of the resistor mix in the insulator bore to assure good electrical contact with the terminal screw. The insulator was loaded by volume to yield 193 $\pm$5 mg of resistor mix and 124 $\pm$5 mg of copper glass. The volume loader was a brass bar, one each for the resistor mix and the copper glass, with a hole bored in it. The material was poured into the hole and the excess was scraped off using a spatula, the edge of which was level on the brass bar. The resistor mix was poured into the insulator on the head of the center wire, the copper glass was poured on top of the resistor mix, and the terminal screw was placed on top, extending above the insulator as shown in Figure 8. This assembly was sealed as described in the next section.

Sealing Apparatus and Procedure

The sealing apparatus was built to individually seal

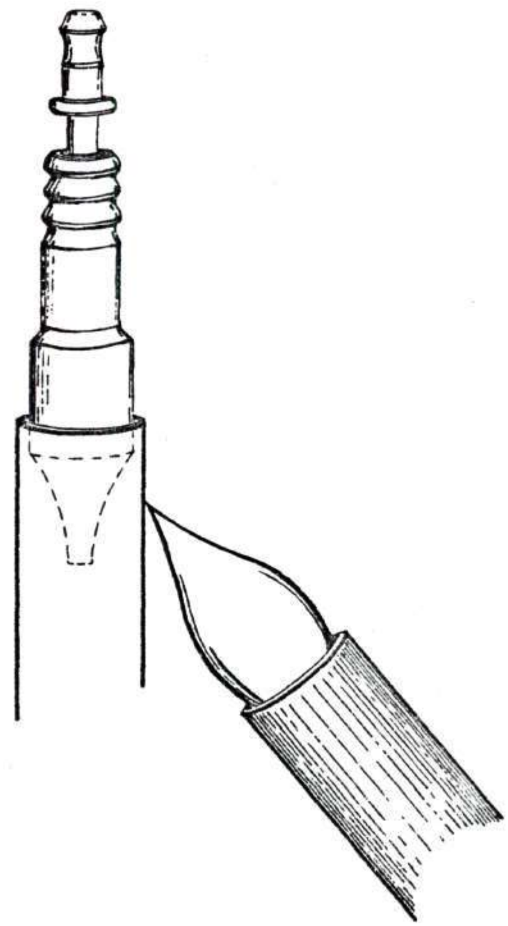


Figure 8. A Schematic Drawing of Sealing a Loaded Resistor Spark Plug.

spark plugs in a manner similar to a large scale process. The times and temperatures of the sealing procedure were selected because they simulated a typical production process. Briefly, the spark plugs were heated for 5 min. 40 sec., cooled for 10 sec. and hot pressed for 28 sec. They were cooled in air to room temperature.

The sealing apparatus is shown in Figure 9. The spark plug sat on a stool (hollow steel cylinder) with three gas-air torches equally spaced around it. Each flame was at an angle of $50\pm5°$ from the horizontal and impinged the stool at 1 cm below the top. Figure 8 shows the spark plug on the stool being heated. For simplicity only one torch is shown.

The temperature was controlled by the pressure of the gas and air going to the torches and the control knobs on the torches were fixed. The air pressure was 12 psi, measured on a 0 to 60 psi pressure guage. The gas pressure was measured by the number of turns of the gas valve which had a very reproducible and linear ratio of number of turns to pressure. A monometer was later installed and used, and the gas pressure was 13 inches of water.

The pressures given above were used because they produced a flame which made the interior of the insulator 975 $\pm15°C$. This temperature was periodically measured using a chromel-alumel thermocouple. The bead of the thermocouple was embedded in the resistor mix of an insulator that had only the center wire and the resistor mix in it. This

(A)

(B)

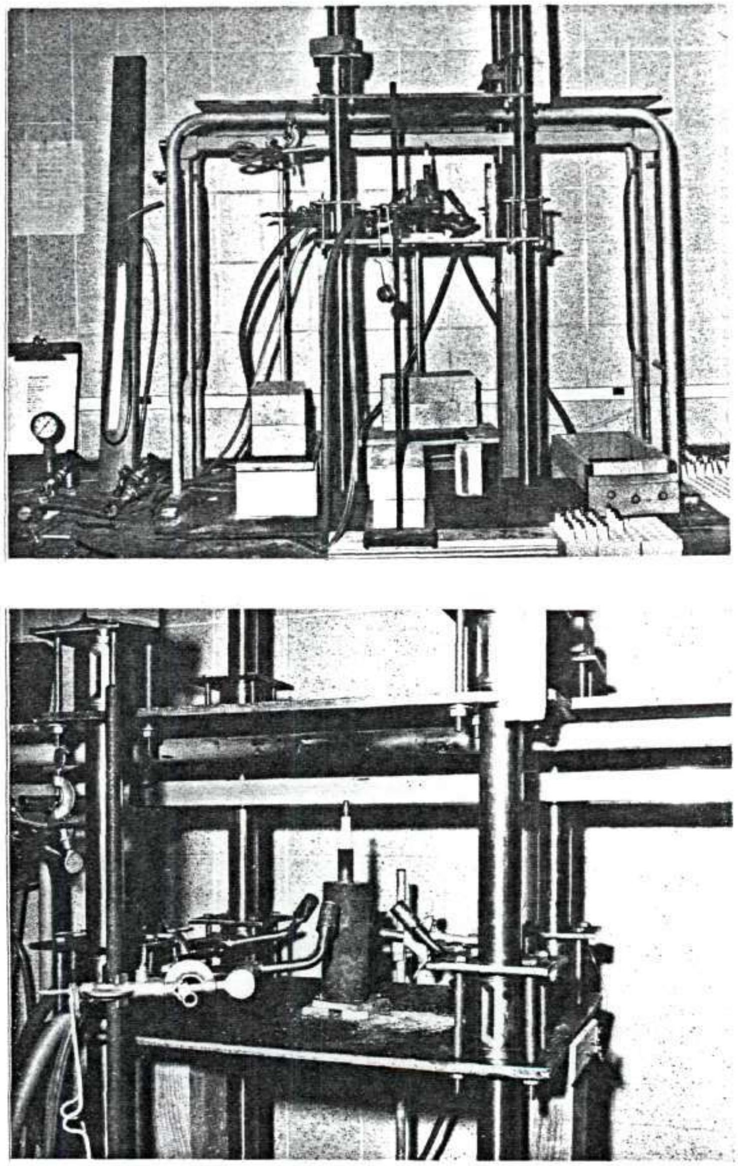


Figure 9. The Apparatus Built to Seal Spark Plugs in a Manner Typical of Production Techniques: (A) General View, (B) Close-Up of the Stool and Torches.

assembly was heated in the sealing apparatus and the temperature was monitored from room temperature to the end of the heating cycle, 5 min., 40 sec. Maximum temperature was achieved between three and four minutes after initial heating.

There was a metal plate located 6 cm above the terminal screw. It weighed 14 kg and could be raised and lowered. It was used to press the spark plugs before heating, which compacted the resistor mix and the copper-glass. This increased the density of the final sealed resistor mix by allowing more pressure to be transmitted through the molten materials during hot pressing. The same plate was used for hot pressing the terminal screw into the insulator.

Three procedures were used for sealing the spark plugs. In all three the spark plugs were pre-pressed on a cool stool. For procedure A, the spark plugs were heated for 5 min., 40 sec., from room temperature to 975 $\pm$15°C. They were cooled for 10 sec. during which time they were transferred to a cool stool. The plugs were hot pressed for 28 sec., removed from the stool, and allowed to cool in air to room temperature. Procedure B was similar to Procedure A, the only difference was that the hot plug was not transferred to a cool stool for hot pressing.

Procedure C allowed continuous monitoring of the spark plug resistance values during the sealing procedure. Before loading, chromel wires were spot welded to the electrodes. These leads were connected to a millivolt recorder with special circuitry and calibration for monitoring resistance. The circuitry is shown in Figure 10, and a typical resistance plot is shown in Figure 11. Otherwise, Procedure C was the same as Procedure B.

Resistance Values

The millivolt recorder was calibrated from 100 to 10 mV as 0 to 100 kΩ, respectively, using a standard resistance box. Resistance values greater than 100 kΩ (from 0 to 10 mV) were not measured, but designated as >100 kΩ. The sealed plugs were allowed to cool at least three hours before the room temperature resistance values (R_{RT}) were measured using the millivolt recorder. The mean, $\overline{X}$, and the standard deviation, σ, were calculated for the final resistance values of each series of plugs containing the same resistor mix. For the standard deviation,

$$\sigma = \left[\frac{1}{n-1}\sum_{i=1}^{n}(X_i-\overline{X})^2\right]^{1/2} \tag{1}$$

When the millivolt recorder was used (Procedure C), the minimum resistance value was also recorded since it varied with some compositional changes. This sealing temperature value (R_{ST}) occurred just before hot pressing.

Attempts were made to reduce the scatter in the resistance values by increasing the B_4C content, reducing the particle sizes of the components, and changing the geometry of the electrodes. Limited success was achieved with the last

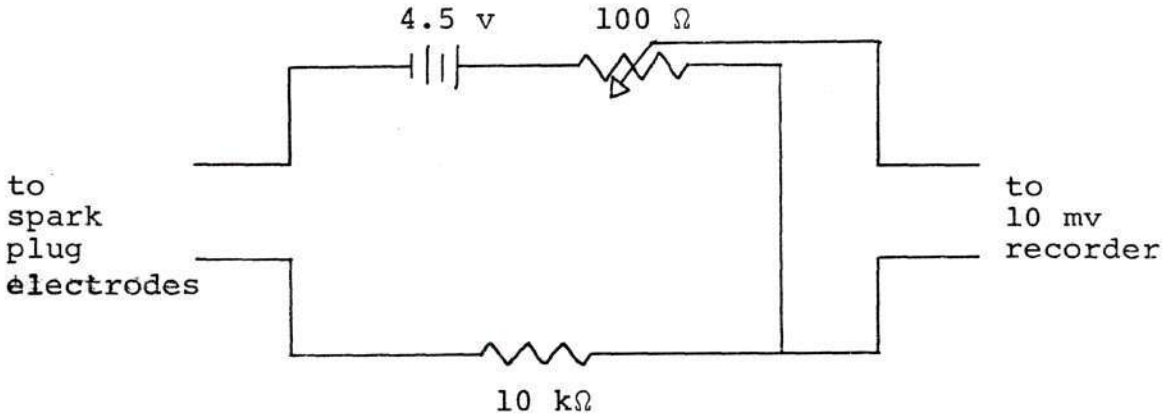


Figure 10. The Circuitry Used to Modify the Millivolt Recorder to Measure Resistance Values of the Spark Plug Throughout the Sealing Process[35].

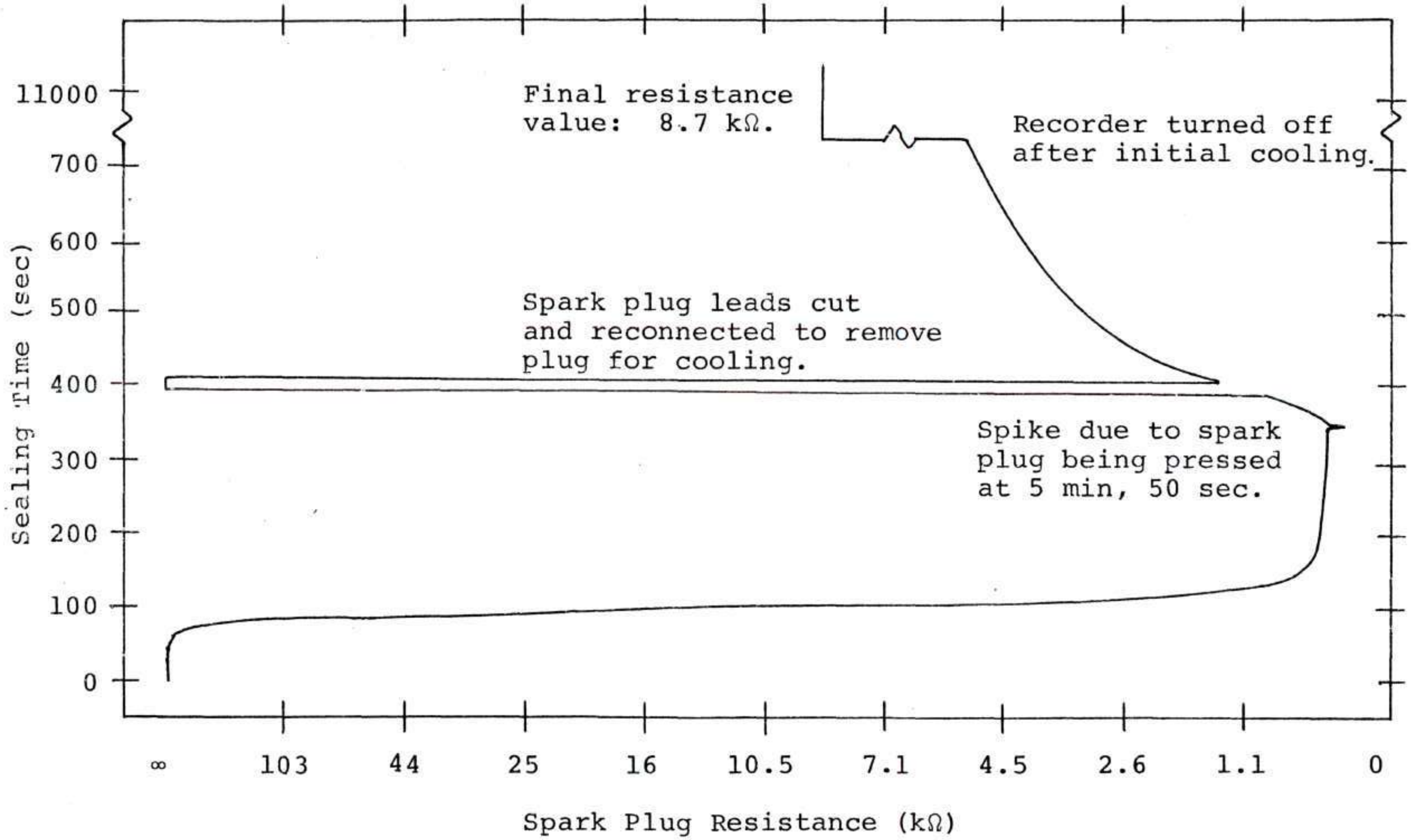


Figure 11. A Millivolt Recorder Plot Calibrated to Measure Spark Plug Resistance Values During the Sealing Process.

method, and the information is given in Appendix C.

Photomicrographs

In order to study the microstructure of the sealed spark plugs, the plugs were sectioned axially, ground and polished, and photographed. Figure 12 is a typical photomicrograph showing both electrodes, the copper glass and the resistor mix.

Figure 12. A Picture Showing the Resistor Component, Copper-Glass and Electrodes Sealed in an Insulator.

CHAPTER IV

RESULTS AND DISCUSSION

Introduction

Trial resistor mix compositions were formulated using some or all of the four components to study the effect of each component on resistance values. Initially, the TiO_2, B_4C and binder (hereafter called modifiers) were added to the glass individually and in pairs. Subsequently, all three modifiers were added to the glass in various proportions. The specific resistor mix compositions, the resulting spark plug resistance values, and a discussion of these results are given in this chapter. Based on the discussion of results and a microstructural examination of the resistor component, a model is postulated for the current flow through the resistor component.

Resistor Mix ID: N, θ, and Q

Titania, B_4C and binder were added individually to the glass for mixes, N, θ, and Q, respectively. The two component compositions and the resulting resistances are shown in Table 5 and Figure 13. (In Tables 5, 6, and 7, R_{RT} is the mean spark plug resistance value at room temperature, R_{ST} is the mean value, if measured, at the sealing temperature, σ, is the standard deviation of the mean, and n is the

Table 5. The Compositions and Resulting Spark Plug Resistances for Two Component Resistor Mixes: N, θ, and Q.

	Weight Percents				Average (kΩ)		
Mix ID	Glass	TiO_2	B_4C	Binder	R_{ST}	R_{RT}	n
	Glass and TiO_2						
N1	93	7	-	-	7.9	>100	2
N2	89	11	-	-	6.6	>100	2
N3	81.3	18.7	-	-	0.4	>100	2
N4	87.8	12.2	-	-	-	>100	3
	Glass and B_4C						
θ1	99	-	1.0	-	3.3	>100	2
θ2	98.5	-	1.5	-	5.0	>100	2
θ3	97	-	3	-	2.6	>100	2
	Glass and Binder						
Q1	95	-	-	5	2.7	>100	2
Q3	85	-	-	15	0.5	>100	2

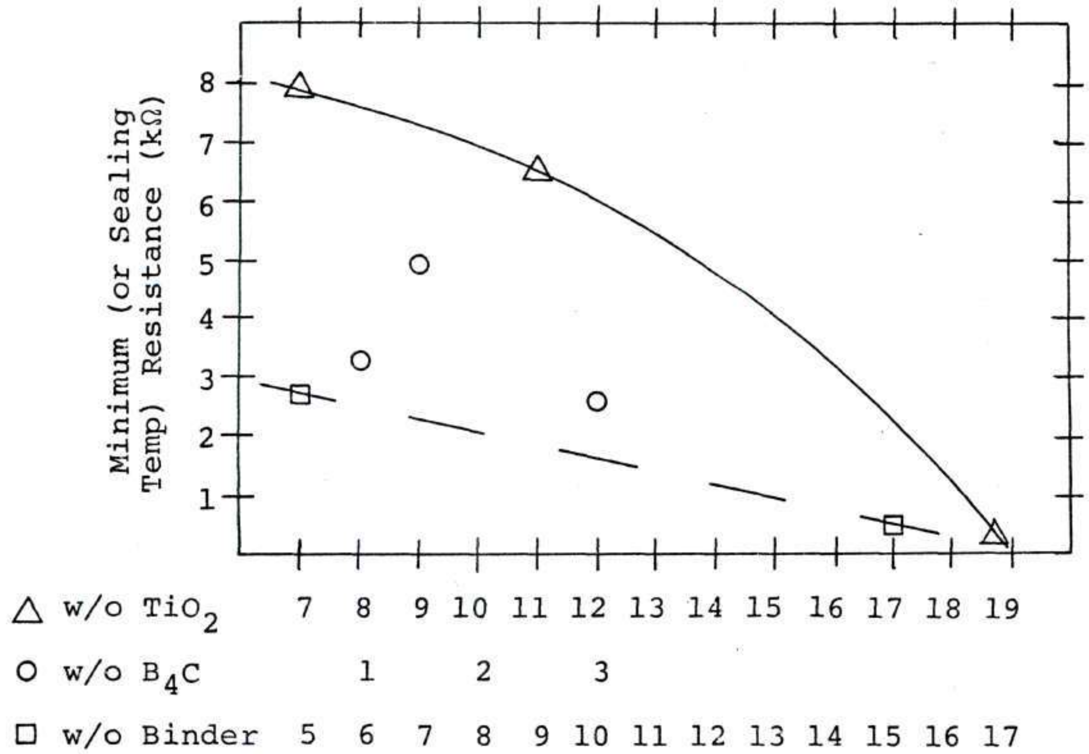


Figure 13. The Minimum Resistance Values Measured During the Heating of Two Component Resistor Mixes: N, Θ and Q.

number of spark plugs that were sealed with each trial resistor mix.) None of the components added individually to glass lowered the room temperature resistance below 100 kΩ. Increased additions of TiO_2 and binder each continually lowered the sealing temperature resistance, but increased additions of B_4C did not show this trend.

Resistor Mix ID: P, R, and S

These mixes had two modifiers added to the glass, TiO_2 and B_4C, TiO_2 and binder, and B_4C and binder, for mixes P, R, and S, respectively. The three component compositions and the resulting resistances are shown in Table 6 and Figure 14. A review of the data in Table 6 shows that TiO_2 must be in the resistor mix to get the resistance values below 100 kΩ. It was tentatively concluded that TiO_2 is the primary conducting medium in the resistor mix, although the B_4C and binder contents do affect the room temperature resistance. Note that some of the data for the P series appear twice in Table 6 to show different trends, i.e., one modifier or ratio of modifiers was held constant while the other increased. The data is similarly arranged for the R series.

Resistor Mix ID: T, U, and V

These mixes contained all three modifiers; in the T, U, and V series, respectively, the binder content, the TiO_2 content, and the B_4C content were varied. The specific compositions and the resulting resistance values are shown in

Table 6. The Compositions and Resulting Spark Plug Resistances for Three Component Resistor Mixes: P, R, and S.

	Weight Percents				Averages (kΩ)			
Mix ID	Glass	TiO_2	B_4C	Binder	R_{ST}	R_{RT}	σ	n
				Glass, TiO_2 and B_4C — B_4C Increasing				
P1	88	11	1	-	0.24	26	16	5
P5	87.5	11	1.5	-	0.13	4	1.1	6
P2	87	11	2	-	0.10	1	0.2	3
				Glass, TiO_2 and B_4C — Increasing B_4C - Higher TiO_2 Content				
P3	80	19	1	-	0.10	5.3	1.2	3
P4	78	19	3	-	0.10	0.22	0.1	2
				Glass, TiO_2 and B_4C — TiO_2 Increasing				
P1	88	11	1	-	0.24	26	16	5
P3	80	19	1	-	0.10	5.3	1.2	3

Continued

Table 6. Continued

Mix ID	Weight Percents Glass	TiO_2	B_4C	Binder	Averages (kΩ) R_{ST}	R_{RT}	σ	n
				Glass, TiO_2 and Binder Binder Increasing				
R1	84.7	10.6	-	4.7	0.77	>100	-	3
R2	80	10.0	-	10	0.50	36	6.1	3
R3	75.5	9.4	-	15.1	0.22	22	5.9	3
				Glass, TiO_2 and Binder Increasing Binder - Higher TiO_2 Content				
R4	75.9	19.0	-	5.1	0.28	>100	-	3
R5	72.0	18.0	-	10.0	0.25	20	5.0	3
R6	67.5	16.8	-	15.9	0.23	5.3	0.4	3
				Glass, B_4C and Binder Binder Increasing				
S1	92.8	-	2.0	5.2	0.98	>100	-	2
S2	88.2	-	1.9	9.9	0.63	>100	-	2
S3	83.2	-	1.8	15.1	0.62	>100	-	3

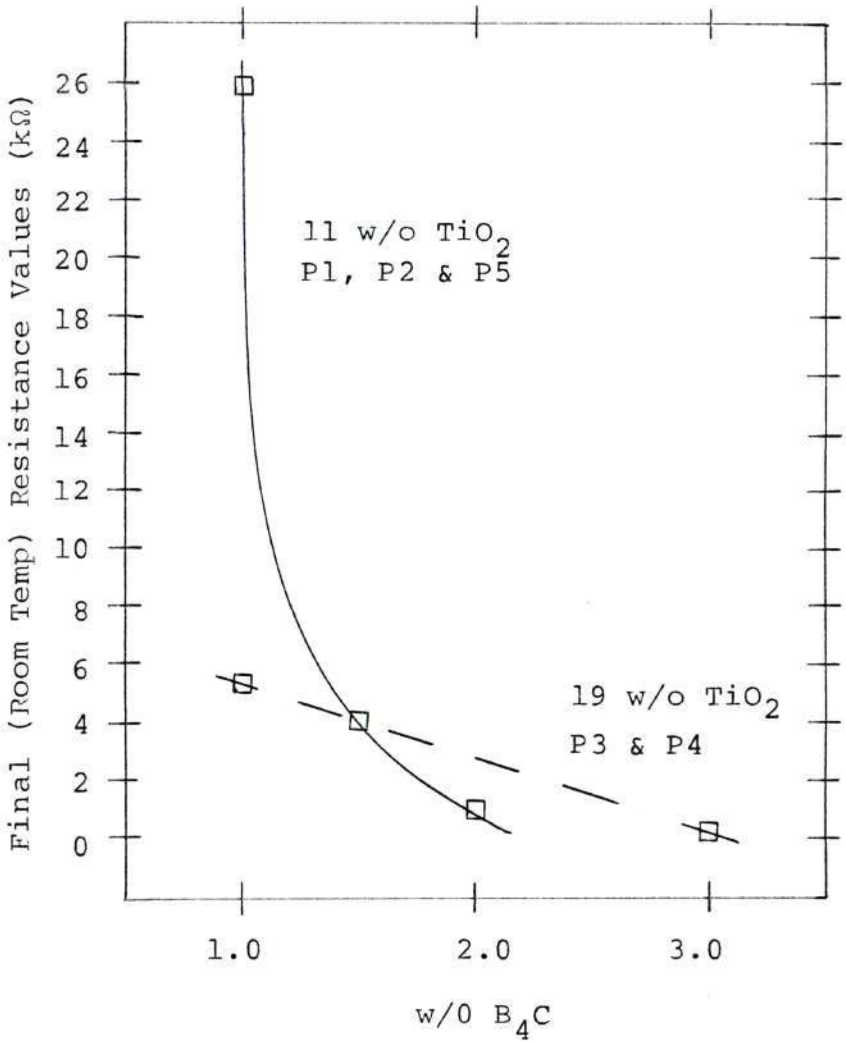


Figure 14. The Final Resistance Values as a Function of w/o B_4C at Two TiO_2 Contents in a Resistor Mix Composed of Glass, TiO_2 and B_4C.

Table 7 and Figure 15.

In the T series, the increase in resistance values as binder was added up to about 6 w/o was not anticipated. Adding binder was expected to reduce the TiO_2, making it more conductive and reducing the overall resistance of the spark plug. This unexpected behavior could possibly be accounted for as follows.

When the binder burned, it combined with oxygen to form SiO_2, CO_2 and water vapor (see Appendix A). The binder first consumed the oxygen in the air in the resistor mix and then attacked the TiO_2 for additional oxygen. At low binder content, the oxygen in the air was sufficient to satisfy the binder so that no TiO_2 was attacked. As it burned the binder left behind small crevices around the resistor mix particles due to the physical absence of some binder molecules. The silica content was also increased. These crevices and additional silica served to increase the resistance value of the resistor mix from 0 to about 6 w/o. Around 6 w/o, there was enough binder to attack the TiO_2 for oxygen. The TiO_2 was reduced and became more (relatively) conductive as the binder content was further increased. As more TiO_2 was reduced, its conductive effect overcame the resistive effect of the crevices and the additional silica, and the resistance value of the mix decreased. Thus, a higher binder content led to low resistance values.

The effect of the binder content between 9 and 15 w/o

Table 7. The Compositions and Resulting Spark Plug Resistance for Four Component Mixes: T, U, and V.

	Weight Percents				Averages (kΩ)			
Mix ID	Glass	TiO_2	B_4C	Binder	R_{ST}	R_{RT}	σ	n
	Increasing Binder, TiO_2/Glass = 0.1257 B_4C/Glass = 0.0171							
T1	87.5	11.0	1.50	0.0	0.07	2.1	1.0	5
T2	84.8	10.7	1.45	3.1	0.08	7.1	4.1	5
T3	82.2	10.3	1.41	6.0	0.16	17.6	10.0	6
T4	79.5	10.0	1.36	9.1	0.18	5.8	2.5	6
T5	77.0	9.68	1.32	12.0	0.18	2.3	1.0	5
T6	74.4	9.35	1.28	15.0	0.35	7.0	7.5	5
	Increasing TiO_2, B_4C/Glass = 0.0171, Binder/Glass = .1153							
U1	82.1	7.02	1.40	9.47	0.21	4.6	1.4	8
U2	79.3	10.0	1.36	9.14	0.26	2.4	0.8	8
U3	76.7	13.1	1.31	8.85	0.25	1.9	1.1	8

Continued

Table 7. Continued

Mix ID	Weight Percents Glass	TiO_2	B_4C	Binder	Averages (kΩ) R_{ST}	R_{RT}	σ	n
	Increasing B_4C, TiO_2/Glass = 0.1396 Binder/Glass ≈ 0.1326							
V2	78.0	10.9	1.00	10.1	-	6.05	3.14	6
V3	77.8	10.9	1.20	10.1	-	3.53	1.52	6
V4	76.9	10.7	1.39	10.9	-	3.00	1.41	6
V5	77.1	10.8	1.59	10.6	-	2.35	1.25	6
V6	77.4	10.8	1.80	10.0	-	1.14	0.40	5
V7	76.8	10.7	2.00	10.5	-	1.90	1.06	6
V8	76.9	10.7	2.40	9.96	-	0.90	0.53	6
V9	76.2	10.6	2.78	9.91	-	0.90	0.40	6
V10	76.3	10.6	3.20	9.87	-	0.58	0.22	6

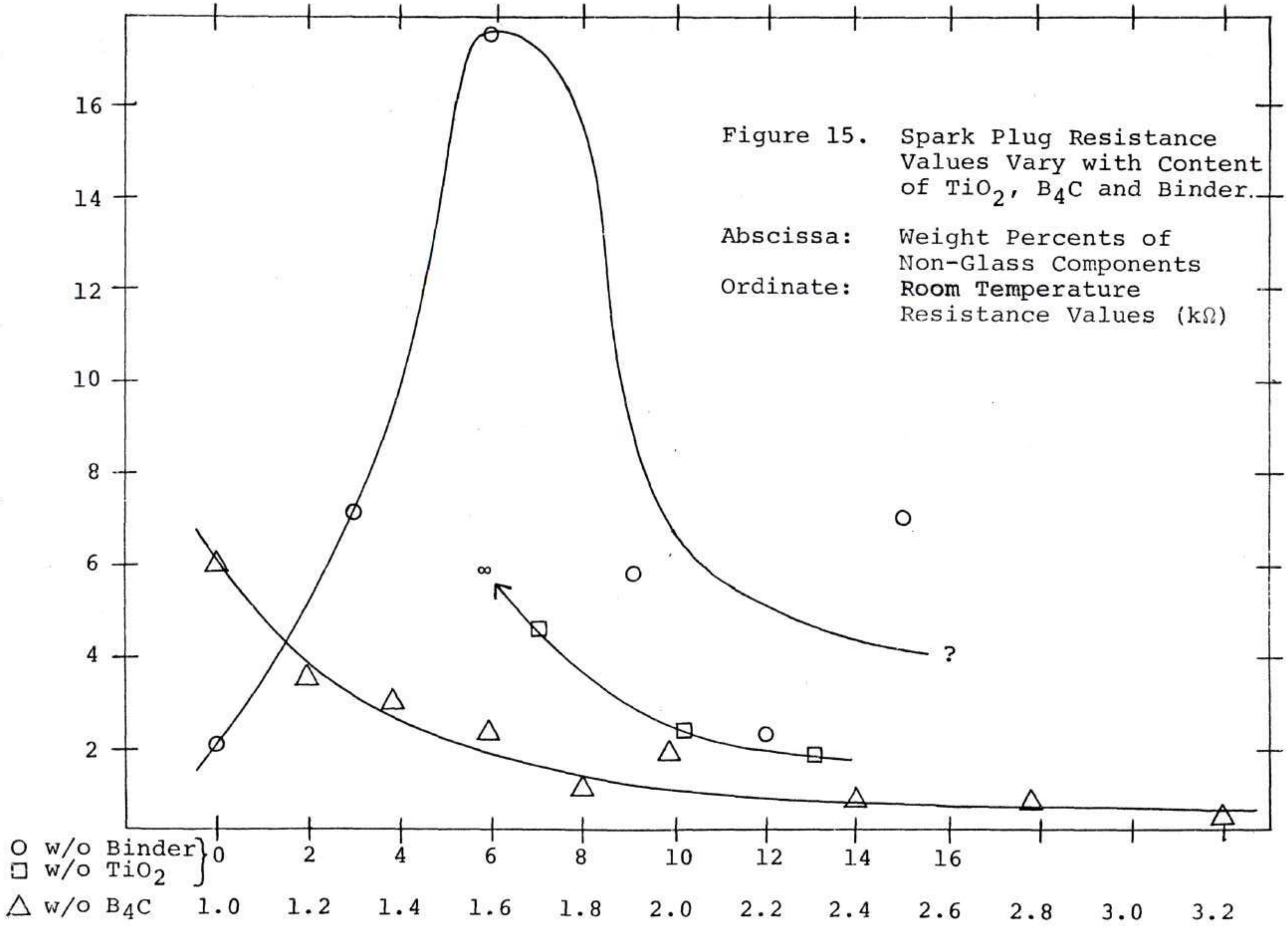


Figure 15. Spark Plug Resistance Values Vary with Content of TiO_2, B_4C and Binder.

Abscissa: Weight Percents of Non-Glass Components

Ordinate: Room Temperature Resistance Values (kΩ) is not certain. The 15 w/o data point is probably in error since this resistance value has a very high standard deviation. Approximately 10 w/o binder was used in all subsequent resistor mixes. This value was enough to insure uniform mixing and above the 6 w/o addition that gave the high resistance values.

In order to determine qualitatively if any binder was not completely burned during the sealing process, five plugs were reheated in the sealing apparatus and visual estimates were made of the amount that the terminal screw rose during reheating. Three of the plugs were from the P2, P3, and P5 lots which contained no binder, and they rose 1/8, 1/16 and 1/8 inch, respectively. This behavior was due to the expansion of trapped gases as well as the expansion of the hot materials. Two of the plugs were from lot T4 which contained 9.1 w/o binder, and they rose 3/16 and 1/4 inch. Since the plugs with the binder rose more during reheating than the plugs without binder, it is assumed that there was residual binder in the resistor mix after the original heating. The effect of the unburned binder on the resistance values is unknown.

In the U series of trial resistor mixes, the effect of the TiO_2 content was studied. The resistance values decreased from 4.6 to 1.9 as the TiO_2 was increased from 7 to 13 w/o. This behavior was expected because of the increasing amount of reduceable TiO_2. A comparison of mixes U2 and T4 shows that the resistance values in the U series were somewhat low, but this was probably due to slighly different sealing conditions as discussed in the procedure.

In Table 3 of Chapter II, the large increase in the conductivity of TiO_2, even at slight reduction, was shown. The S series (Table 6) contained no TiO_2 and all the mixes yielded resistance values >100 kΩ. In Table 7 the amount of TiO_2 is critical below 7 w/o, based on a qualitative comparison of the S series and the U series and on the information referred to in Table 3. The conclusion from this information is that TiO_2 is considered the primary conductor in the resistor mix, with the B_4C and the binder having secondary effects.

Considering that a slight reduction of TiO_2 greatly decreases its resistivity (see Table 3), and considering the decrease in the resistance values due to the addition of TiO_2 (see the S and U series, Tables 6 and 7), it is concluded that the TiO_2 is reduced during the sealing procedure. The extent of the reduction is assumed to be slight, but the amount is unknown.

In the V series, the B_4C content was not studied below 1 w/o because there may be a problem of effectively dispersing the B_4C particles. The effect of changing the B_4C content on the resistance values was greatest around 1 w/o and resistance values were almost independent of B_4C content above 1.8 w/o. The B_4C curve in Figure 15 agreed well with expectations based on the P series. According to Figure 6, the resistivity of B_4C is about 1Ω-cm at room temperature and so this component adds significantly to the conduction of the resistor mix.

Microstructural Examination of the Resistor Component and the Copper Glass

This discussion is an analysis of the microstructure of the resistor component and the copper glass of a sealed spark plug. Typical photomicrographs, shown in Figures 16, 17, and 18, reveal a laminar geometry of the resistor component. The photomicrographs are oriented with the terminal screw above (at the top of the page) and the center wire below (at the bottom). In each figure, part (a) is a light field view and part (b) is a dark field view, which allows subsurface observation.

The photomicrographs of the microstructure revealed that a laminar flow of the resistor mix occurred during hot pressing when the material was extruded up around the terminal screw and down around the center wire. Between the electrodes, the flow was approximately parallel to the center wire head, and on the outer edges, the flow was parallel to the insulator walls, as shown in Figure 12. The laminar flow consisted of alternate layers of glass and TiO_2, with B_4C particles and pores randomly oriented in the flow matrix.

The dark field views particularly reveal the laminar pattern. During the heating period, the glass particles softened enough to be deformed and to flow during hot-pressing.

(a)

(b)

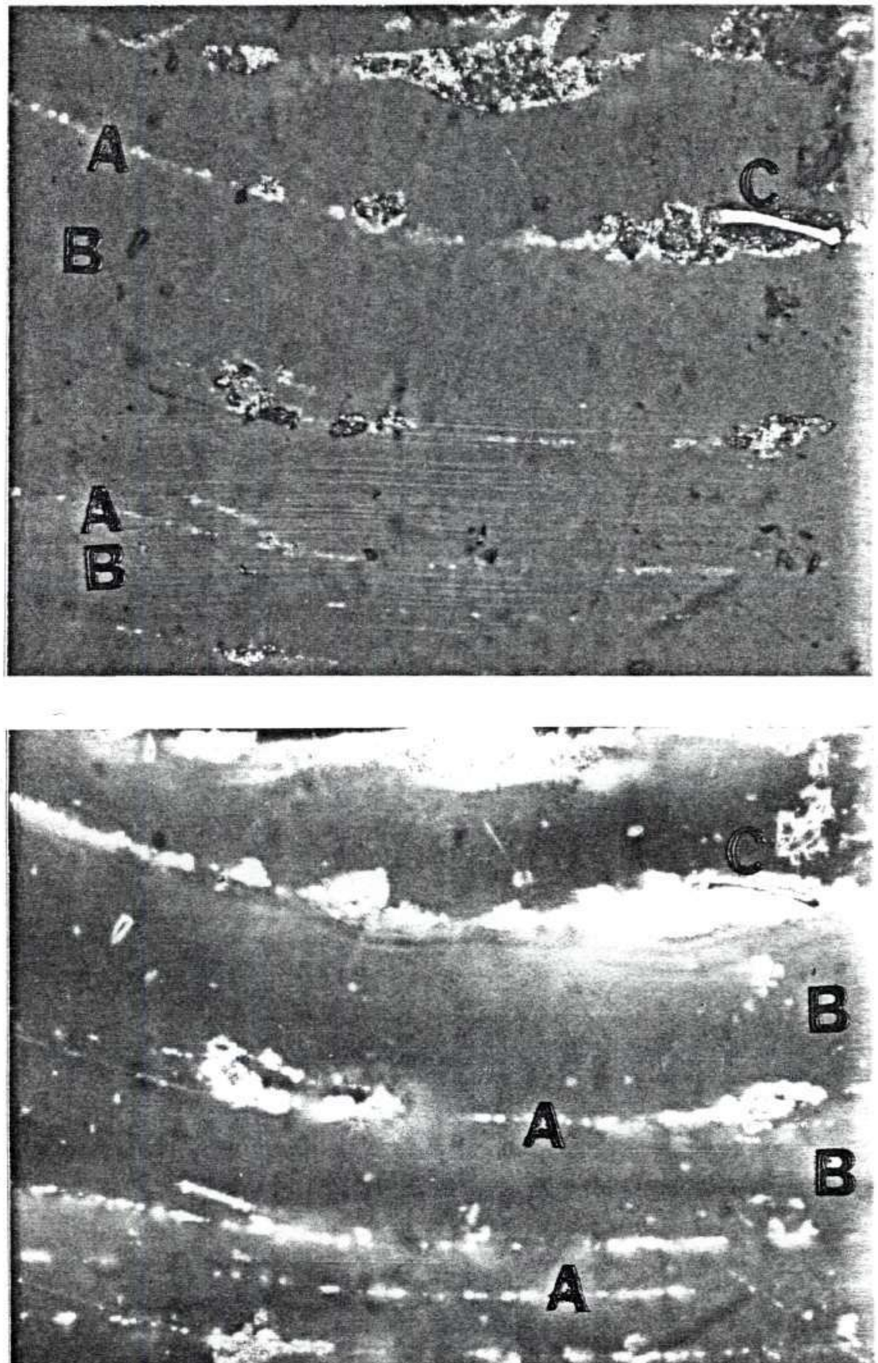


Figure 16. Photomicrograph of a Sealed Resistor Component Revealing that Laminar Flow of the Material Occurred During Hot Pressing: (A) TiO_2 Layers, (B) Glass Layers, (C) B_4C Particles (542x).

(a)

(b)

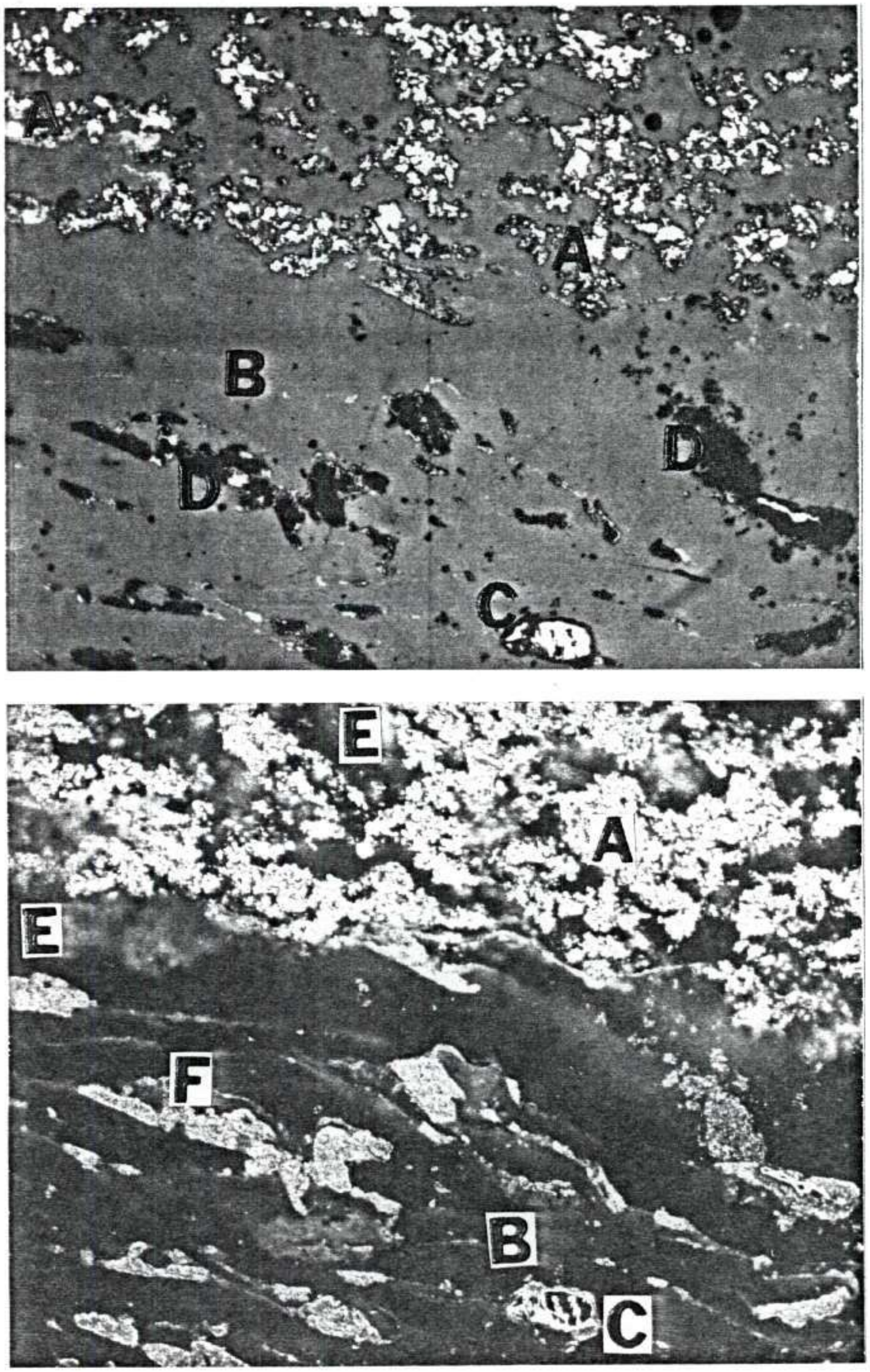
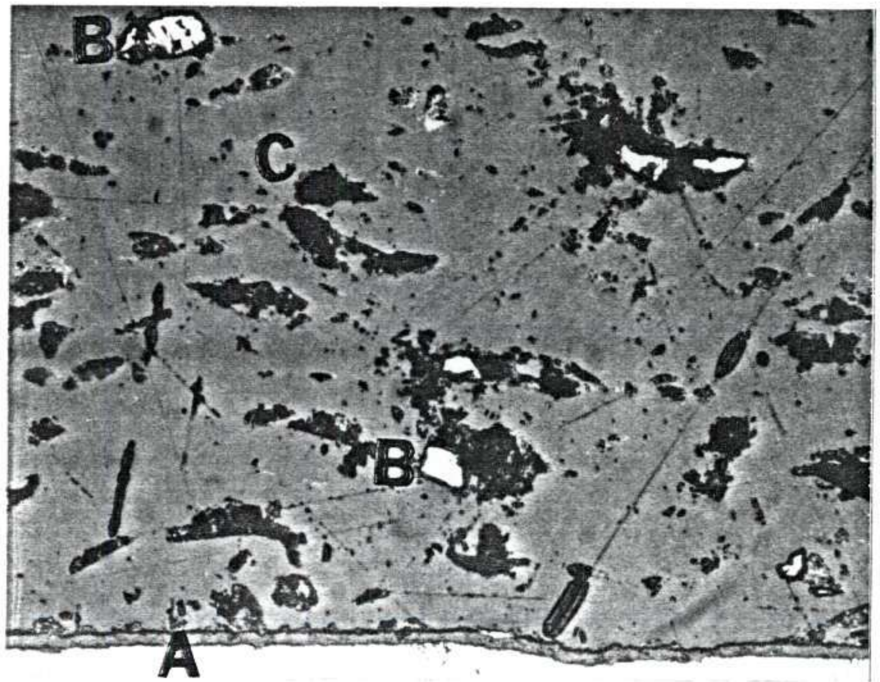


Figure 17. Photomicrograph of a Sealed Spark Plug Showing the Copper-Glass and the Resistor Component: (A) Copper-Glass, (B) TiO_2 Layers, (C) B_4C Particle, (D) Pores in the Glass-TiO_2 Matrix, (E) Copper-Glass Below the Surface of the Sample, (F) TiO_2 in the Pores (196x).

(a)



(b)

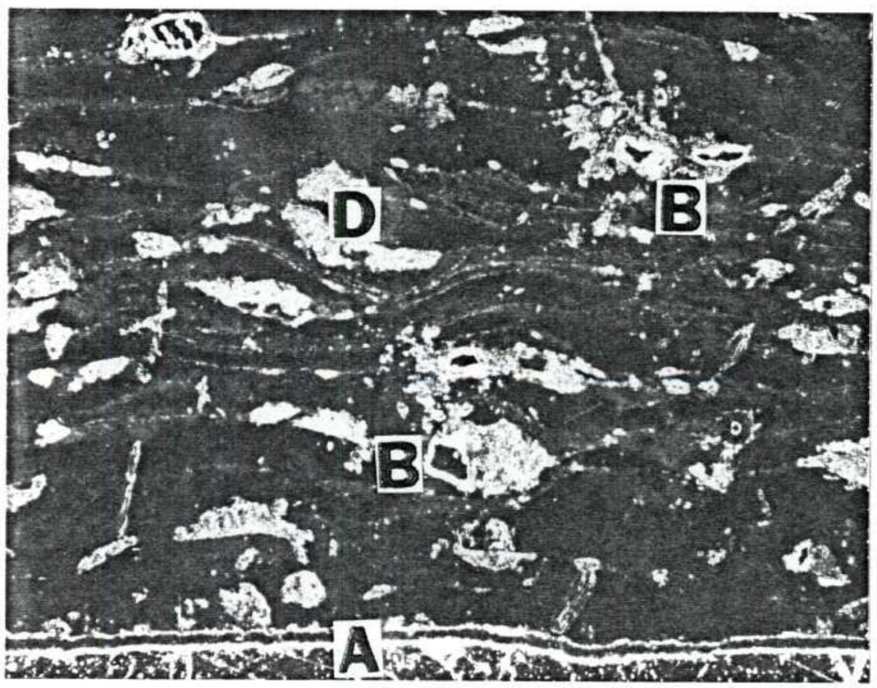


Figure 18. A Photomicrograph Showing the Interface Between the Sealed Resistor Component and the Center Wire Head: (A) Center Wire Head, (B) B_4C Particles, (C) Pores in the Glass-TiO_2 Matrix, (D) TiO_2 in the Pores (196x).

Heating was insufficient for the glass particles to flow to the extent of removing all grain boundaries. In Figure 16, the TiO_2 is seen in alternate layers with the glass. The TiO_2 layers are in the glass grain boundaries but are not continuous because the glass separates some of the individual particles and conglomerates.

All three figures show pores and B_4C particles randomly orientated in the glass matrix. In some cases, the pores are like crevices which are deformed parallel to the glass. Some TiO_2 can be seen in the pores at 542x (Figure 16), and when the pores were examined at 945x, TiO_2 particles were seen as lining on the surfaces of the pores. There were several possible causes of the formation of the pores. Pieces of glass may have been "pulled out" of the sample during grinding. The pores may have been pockets of trapped gases created by the decomposition of the binder or air that became trapped as the glass softened.

The interface between the copper glass and the resistor mix as shown in Figure 17, had no distinct boundary. The dark field view shows the copper particles below the surface, and the copper appears to make a continuous path from the resistor mix to the terminal screw.

The interface between the center wire head and the resistor mix, as displayed in Figure 18, shows some type of layered material on the surface of the center wire head, which may be an oxidation layer. Otherwise, there appears little, if any, reaction among the components.

At least eight B_4C particles can be seen in the photomicrographs in Figure 18. Particularly the one in the upper left corner and the two in the lower middle section are in positions associated with several layers of TiO_2. Note the overlap of the lower right part and upper left part of Figures 17 and 18, respectively.

Model for Current Flow Through the Resistor Mix

Based on the discussion of the compositional effects on resistance and on the microstructureal examination, a model is postulated to explain the role of each component in the conduction of the electric current through the resistor component. Several further conditions for the model follow. Measurements for the dimensions of the components after being sealed in the insulator were estimated from the photomicrographs. The TiO_2 layers are 0.5 to 3 μm thick and are assumed to be electrically continuous. There are some agglomerates of TiO_2 that have larger dimensions. The B_4C particles are 10 to 30 μm in size and the glass layers are 10 to 50 μm thick. Before sealing, the resistor mix powder consisted of agglomerated fragments of glass, each generally surrounded by a thin layer of TiO_2, with a few B_4C particles dispersed among the glass pieces. In Appendix D, a calculation shows that there is enough TiO_2 in the resistor mix to create the number of TiO_2 layers shown in the typical photomicrographs.

In the model, current flows through the terminal screw and the copper glass with negligible resistance, and it can flow from the copper glass to the resistor mix at any mutual contact point. Each layer of glass in the resistor mix is an insulator and each layer of TiO_2 acts as a conducting path. The pores are resistors but the TiO_2 particles lining the pore surfaces act as conductors. The B_4C particles are also conductors. The resistor matrix is then a circuit of conductors in series and in parallel.

Further, a piece of glass deforms horizontally between the electrodes during the hot-pressing, and the fine TiO_2 particles form broad layers in the glass grain boundaries. The current flows on these TiO_2 layers and through the B_4C particles which are in the grain boundaries in the glass matrix. The coarse B_4C particles are too hard to deform, but the size of the particles allows the "connecting" of several layers of TiO_2. This "connecting" behavior occurs where the B_4C particle size is similar to the thickness of the glass layers, as shown by the dimensions given above. The TiO_2 is the primary conducting medium because it flows and spreads into layers with the glass. The B_4C is also significant because of its "connecting" function. The laminar matrix that forms parallel to the insulator walls is similar to the matrix between the electrodes except for orientation.

A simple schematic of the resistor mix between the electrodes and a similar model of the resistor mix next to the walls of the insulator bore are shown in Figure 19. The glass

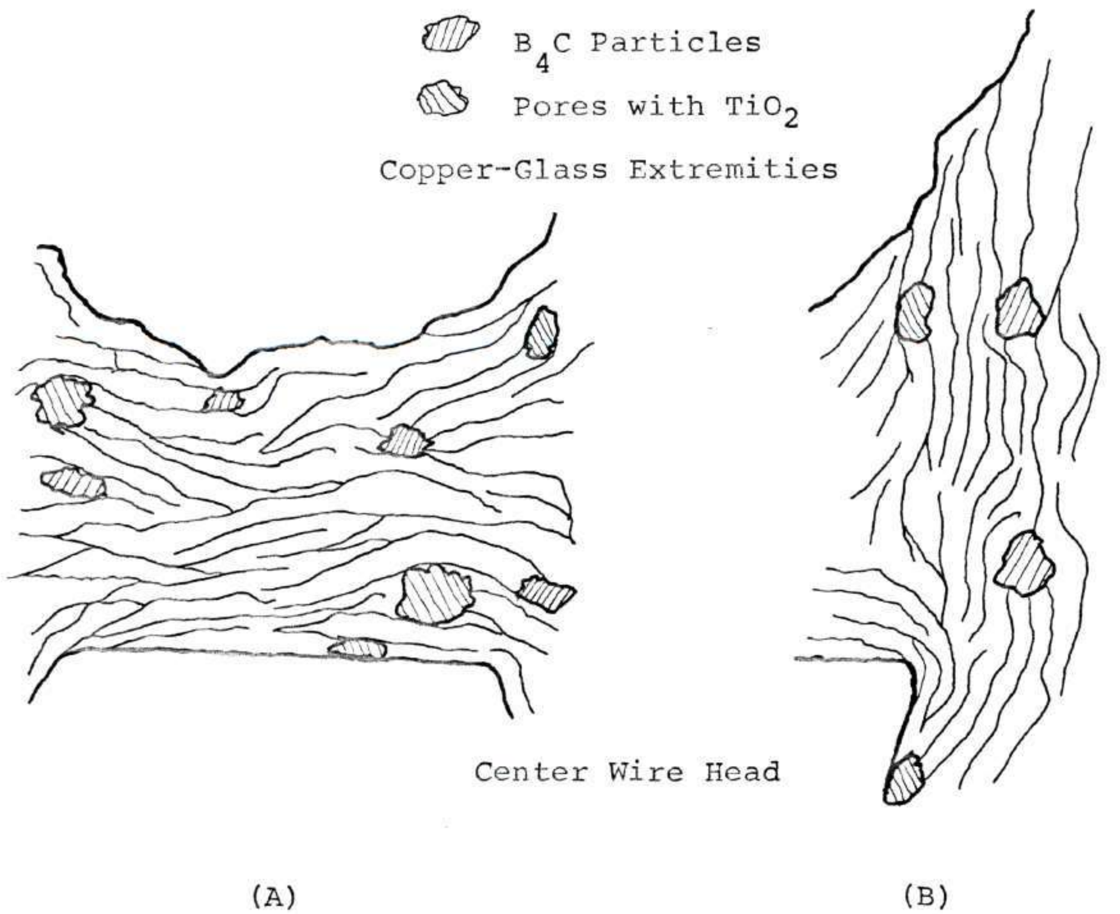


Figure 19. A Schematic Drawing of the Resistor Component Showing Possible Current Paths Through (A) The Area Between the Electrodes and (B) The Area Along the Edges of the Insulator Bore.

is represented by the clear, unmarked background. The lines are the layers of conducting TiO_2. For simplicity they are drawn continuously indicating that the horizontal layers of TiO_2 are assumed to be electrically continuous. The B_4C particles and the pores are shown as labeled. The current flows from the copper glass to the center wire head through the shortest paths. It flows along the TiO_2 layers, through the B_4C particles and around the pores on the TiO_2 that lines the pores.

The role of the binder in the current flow is not known at this time. Evidence was shown which suggests that some unburned binder remains in the resistor mix after the initial heating. Also, the burned binder produces some silica and carbon, and possibly some pores. Because of these uncertainties, no attempt is made in this model to define the role of the binder in the conduction of the electrical current through the resistor. The model does assume that the binder serves to reduce the TiO_2 during the heating cycle. This conclusion is based on a comparison of the N and R mixes which shows that the addition of the binder to glass and TiO_2 reduced the resistance values from infinity to as low as about 5 kΩ.

Discussion of the Model

This discussion shows how the proposed model agrees with the data in Tables 5, 6, and 7. In the N mixes (Table 5), as much as 18.7 w/o TiO_2 was added to the glass with no resulting resistance values below 100 kΩ. In the P mixes (Table 6), 11 w/o TiO_2 and 1 w/o B_4C lowered the resistance values to 26 kΩ. This behavior shows the "connecting" effect of the B_4C as proposed in the model. In the R mixes (Table 6), 10 w/o TiO_2 and 10 w/o binder lowered the resistance values to 36 kΩ. Thus the binder reduced the TiO_2 to the extent that the "connecting" function of the B_4C was not necessarily needed to lower the resistance values below 100 kΩ.

The data provided by the R and S mixes (Table 6) showed that, even without any B_4C, the TiO_2 and binder contents can be increased enough to lower the resistance values to about 5 kΩ. But if the TiO_2 is completely removed, the resistance values of the samples containing B_4C and binder will be >100 kΩ (for the compositions tested in the S mixes). In the proposed model, at a high TiO_2 content, there would be enough conducting layers for the current to flow to the center wire without any B_4C particles. If only B_4C were present, the particles would be isolated by the glass and the resistance would be very high. In a mix with all three modifiers, less than 2 w/o B_4C is effective in reducing the resistance values because the B_4C connects several layers of conducting TiO_2.

The gap between the copper-glass and center wire head is short compared to the distance along the insulator bore from the side of the copper-glass to the side of the center wire. But, in the gap, the laminar flow is perpendicular to the shortest current path distance, and so the current must "zigzag" on the conduction paths around the glassy grains.

On the contrary, the laminar flow pattern adjacent to the insulator walls is parallel to the shortest direction of current path, as shown in Figure 19. So, the current can flow relatively straight to its destination. Information in Appendix C shows that there is no correlation between spark plug resistance values and the gap distance between the copper glass and the center wire head. According to this model, "all" of the volume of the resistor material contributes to the measured resistance value and, hence, the total resistance is relatively insensitive to dimensional variations in the bore of the insulator and metal electrodes.

CHAPTER V

CONCLUSIONS

In this study the compositional effects on the resistance value were investigated for a prototpye resistor mix consisting of approximately 80 w/o of a borosilicate glass with additions (called modifiers) of titania, boron carbide and binder. During the heating and sealing the hot extrusion of the mix resulted in a laminated structure of the resistor mix components. The influences of composition on resistance are listed initially and then combined with the directional macroscopic nature of the material to provide a model for the bulk resistance behavior.

1. When the modifiers were added individually to the borosilicate glass, none of the final resistance values could be lowered below 100 kΩ within the ranges of compositions studied.
2. When the modifiers were added in pairs, titania had to be one of the components in order to produce final resistance values below 30 kΩ.
3. In compositions containing no binder the introduction of B_4C particles was very effective in reducing the final spark plug resistance to values below 10 kΩ.
4. In resistor mixes containing no B_4C particles more than

15 w/o each of TiO_2 and binder were necessary to achieve resistance values of 5 kΩ.

5. The TiO_2 is the primary conductor and the B_4C is the secondary conductor in the resistor component.
6. In compositions containing all components, the additions greater than 5 w/o of the silicone resin base binder appeared effective in lowering the resistance value. This behavior undoubtedly occurred because of the reduction of the titania, which made this component more conductive.

Based on the microstructure examination of the prototype resistance after sealing the following conclusions were made.

7. During the sealing process the resistor mix was extruded from between the electrodes up around the top terminal screw and down around the head of the center wire.
8. During extrusion a very laminar structure was formed consisting of elongated glass grains coated with the titania powder. The glass was oriented perpendicular to the electrodes between the electrodes and parallel to the electrodes along the bore wall of the insulator.
9. The conduction paths for the current through the resistor mix from the terminal screw to the center wire head consist of electrically continuous layers of TiO_2 alternating with layers of glass. The B_4C is dispersed randomly in the resistor mix acting as connecting points between the layers of TiO_2.

10. The B_4C particles served to provide conducting links between the layers of titania powder and, hence, increasing the number of particles was effective in reducing the resistance values.

11. The anisotropy of the resistor macrostructure effectively served to minimize variable resistance values caused by non-uniform dimensions on the various components of the spark plugs. For example, the information in Appendix B shows no correlation of the gap distance between the copper glass and center wire and the measured spark plug resistance values.

APPENDIX A

HEAT TREATMENT INFORMATION DOW CORNING RELEASE COATING Q1-2531

The binder used in the resistor mixes that were formulated in this investigation was Dow Corning Release Coating Q1-2531 (lot # BH026036). The material is a silicone resin binder and the composition is proprietary. When heated from room temperature to 800°C for three hours and then held at 800°C for one hour, the binder is known to transform to silica, carbon dioxide, water vapor and possibly some other carbonaceous materials.[36] The following equation is postulated to describe the decomposition of the binder:

$$SiO(CH_3)_2 + 4O_2 \xrightarrow[\text{heat}]{} SiO_2 + 2CO_2 + 3H_2O \qquad (2)$$

Two tests were done to consider if Equation (2) is a reasonable, qualitative statement of the decomposition of the binder due to heat treatment. The molecular weights of $SiO(CH_3)_2$ and SiO_2 are 74 g/mole and 60 g/mole, respectively. If Equation (2) is correct, then the binder should transform to silica after sufficient heat treatment. In other words, the weight of material in a crucible should change from 74 g/mole to 60 g/mole, a 19 w/o loss.

The binder was prepared in the following manner for both tests. The binder was dried in an aluminum foil container in an electric dryer at 160°F for about three days and then dried in air for about one week. The dried binder was pulled off the aluminum foil and kept in air for the two tests.

The first test considered long term heating of the dried binder. The binder (1.54 g) was put in a porcelain crucible and heated in an electric furnace at 427°C for about 24 hours. After the heat treatment, the remaining material weighed 1.24 g, for a 19.5 w/o loss.

In the second test, the binder was heated for short periods of time typical of the sealing procedure. The dried binder was not brittle, so it was thermally treated in liquid nitrogen to harden the resin, and then crushed and sized. The size ranges were +12 mesh, -12 to +20 mesh, and -20 to +35 mesh, and the following respective amounts of each size were put in six porecelain crucibles: about 0.121 g, about 0.243 g, and about 0.106 g. The total amount in each crucible averaged 0.470 g. The sizing and weighing was done to get approximately uniform binder surface area in each crucible. The six crucibles were heated individually in an electric kiln at 982°C for from one to six minutes. The remaining material was weighed and the percent weight losses as a function of heating time are shown in Figure 20.

The results of these two tests show that about 20 w/o material is lost during heat treatment of the binder, and this amount is consistent with Equation (2). Other information to consider is that water was observed dripping from the hollow

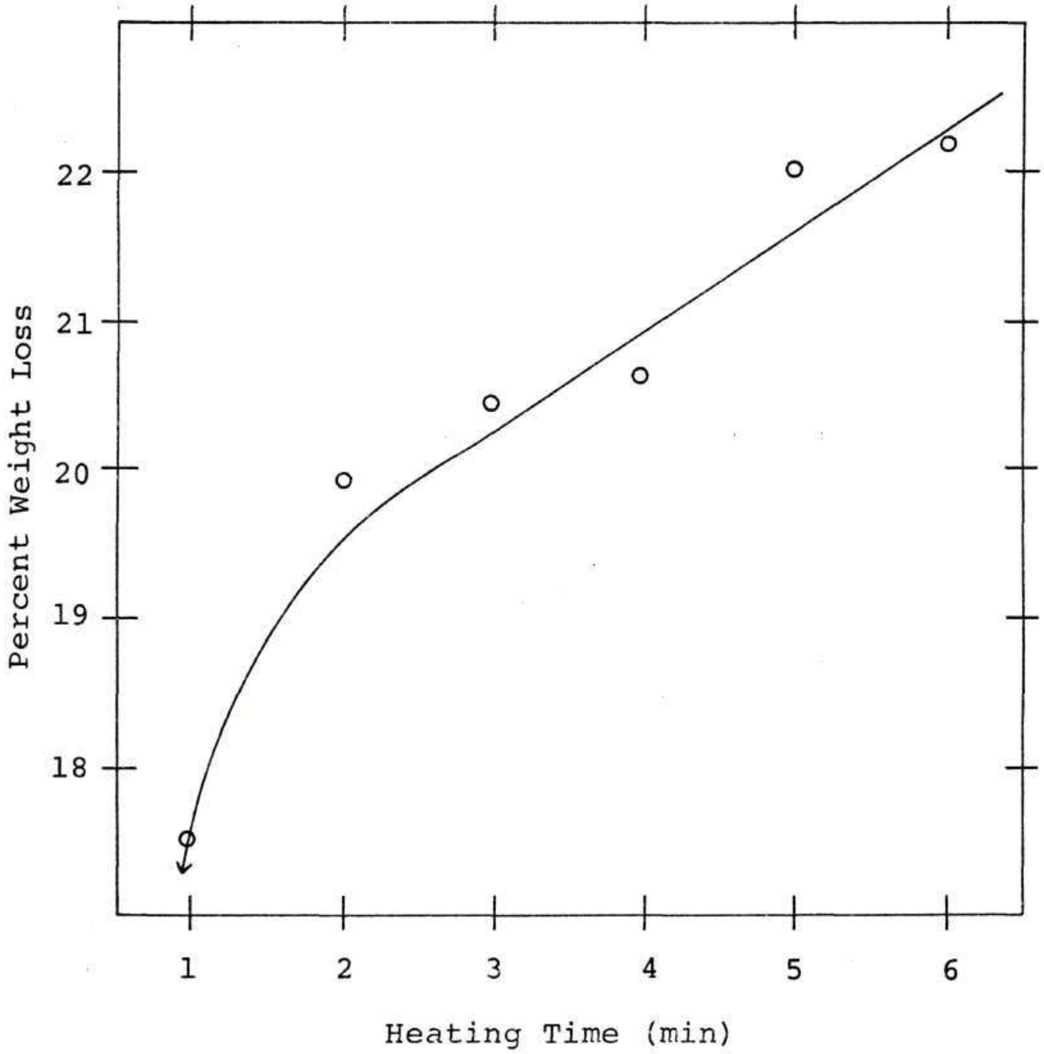


Figure 20. The Weight Loss of Binder Due to Heat Treatment at 982°C.

stool that held the spark plugs during the sealing procedure. The conclusion is that Equation (2) is an approximate statement of the effect of heat treatment on the binder.

APPENDIX B

A DESCRIPTION OF THE SPARK PLUG INSULATOR, ELECTRODES AND COPPER-GLASS

Spark plug insulators, terminal screws, and center wires were obtained from a spark plug manufacturer, and they are pictured in Figure 21. The insulator is a high alumina body with a small shoulder in the lower part of the bore on which the center wire head rests when it is placed into the bore. The terminal screw is C1008 steel with a nickel flash coating. The terminal screw has coaxial grooves on its lower end so that a firm mechanical seal between the copper glass and the grooves is created when the sealed plug cools. The center wire is made of inconel 600. The center wire head is shaped like a parallelepiped and has two grooves crimped in it on both long sides. The grooves and the shaped head prevent the center wire from turning in the sealed plug.

The copper glass was also obtained from a spark plug manufacturer. It consists of 40 w/o glass and 60 w/o copper powder. The composition of the glass is 69.9 w/o SiO_2, 25.7 w/o B_2O_3, 2.9 w/o Al_2O_3 and 2.0 w/o Na_2O.

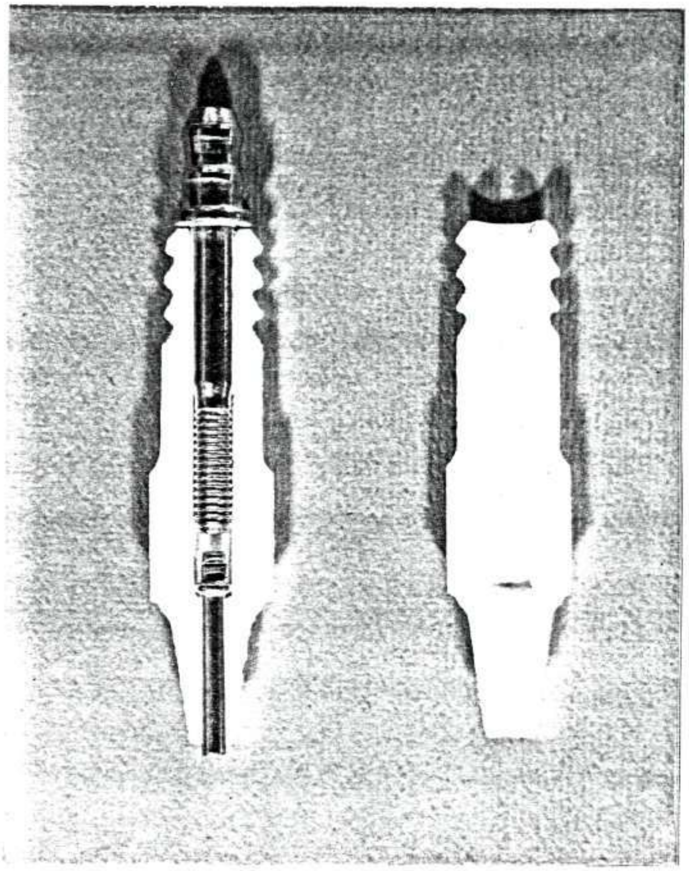


Figure 21. The Spark Plug Electrodes and Insulator Showing the Shoulder on Which the Center Wire Head Rests in the Lower Part of the Bore.

APPENDIX C

ATTEMPTS TO REDUCE THE SCATTER IN THE SPARK PLUG VALUES

The scatter in the spark plug resistance values as shown by the standard deviations is not desireable. The scatter can be studied by considering the ratio $\sigma/\overline{X}$, where σ is the standard deviation and $\overline{X}$ is the mean of a sample of plugs. Four tests were made to determine the cause of the scatter and find a way to reduce it. The tests were (a) to correlate the resistance values with the distance between the copper glass and the center wire (hereafter called the gap distance), (b) to increase the B_4C content, (c) to reduce the particle size of the three dry components, and (d) to consider different electrode geometries.

In order to determine if there was a correlation between the resistance values and the gap distance, thirteen spark plugs of the same composition were sectioned and polished as described in Chapter III. The resistance values were measured before and after the sectioning process. Photomicrographs were made at 50x and the gap distance was measured at eleven equally spaced positions across the photomicrograph. There was no correlation between the resistance values and the gap distance as can be seen in the data in Table 8. These results show that the scatter in the resis-

Table 8. The Lack of Correlation Between Resistance Values and the Gap Distance.

Plug ID	R_{RT}	R_C	$\overline{X}$	T
8	5.4	17.0	58	7.17
3	7.7	15.0	28	2.3
6	6.5	13.8	36	3.0
4	6.4	13.2	27	2.4
1	7.8	12.8	35	3.1
2	7.7	11.4	42	3.7
5	6.7	11.0	35	3.1
7	5.4	9.4	36	3.1
11	4.0	6.8	36	3.1
10	4.0	6.3	37	3.4

R_{RT}: The room temperature resistance value of the sealed plug (kΩ)

R_C: The resistance value of the sealed plug after sectioning (kΩ)

$\overline{X}$: The average measurement of 11 distances (x_n) across the gap (millimeters at 50x)

T: Since resistance is proportional to length and since parallel resistors add inversely, then

$$1/T = 1/x_1 + 1/x_2 + 1/x_3 + \ldots + 1/x_n$$

tance values is not due to variable gap distance. Similarly, the results show that the resistance values are not linearly dependent on the gap distance. This last result suggests that the conduction path is not just across the gap but also through the resistor material that is adjacent to the insulator walls.

A possible contribution to the scatter in the resistance values may be the low B_4C content. The B_4C particles may have been poorly dispersed and, if so, the resistor mixes were inhomogeneous. In order to possibly solve this problem, a series of trial resistor mixes were formulated with the B_4C content varying from 2.7 to 3.6 w/o. These amounts were up to about three times as much B_4C as was used in previous trial compositions. It has been shown in Table 7 that increasing the B_4C content lowers the resistance values. Therefore, for this test, the TiO_2 content was reduced in order to balance the effect of the B_4C increase on the resistance values.

The compositions of the resistor mixes and the resulting resistance values are given in Table 9. There is 10 w/o binder in all the compositions and the amount of glass is the balance for 100 w/o. As the B_4C content was increased for each amount of TiO_2 (5, 6.5 and 8 w/o), the ratio $\sigma/\overline{X}$ had no consistent trend. If anything, the scatter in the resistance values increased instead of decreased as the B_4C content was increased. The apparent result of this experiment

Table 9. The Composition of the Resistor Mixes and the Resistance Values of the Spark Plugs Incorporating These Mixes.

Mix ID	w/o B_4C	w/o TiO_2	$\overline{X}$	σ	n	$\sigma/\overline{X}$
U4	2.8	5	51	24	6	0.47
U7	3.2	5	36	14	5	0.39
U10	3.6	5	18	12	4	0.67
U5	2.75	6.5	51	30	5	0.59
U8	3.14	6.5	27	17	6	0.63
U11	3.53	6.5	35	44	5	1.3
U6	2.7	8	35	15	6	0.43
U9	3.09	8	8	3	5	0.41
U12	3.47	8	16	10	6	0.63

was that increasing the B_4C content did not reduce the scatter in the resistance values as measured by the ratio $\sigma/\overline{X}$.

Some of the scatter in resistance values may have been due to laminar flow, and this test was an attempt to reduce the laminar flow by using a smaller particle size for the glass, TiO_2 and B_4C. The composition was the same as resistor mix T4. The three dry components were mixed by hand and then ground and mixed in a Bleuler Mill (model 1193 LOS1659) for one minute. The binder, (2.50 g) was diluted with 9.70 g of acetone to facilitate the dispersement of the binder in the small size mix.

Seventeen plugs were sealed with this mix and the average resistance value was 37.6 kΩ. The standard deviation was 17.1 so that the ratio $\sigma/\overline{X}$ was 0.45, a high value. The reason for this behavior is not understood at this time. Low resistance values were anticipated because reducing the particle size was expected to create many more conduction paths, thus reducing the resistance values. Further, increasing the number of conduction paths was expected to make the resistance values more uniform because a few highly conductive and/or highly resistive paths would have less effect on the overall resistance value.

Some of the scatter in the resistance values may have been due to varaible bonding between the electrodes and the resistor mix and/or the copper glass. The following changes in the electrode geometries were made in order to reduce this effect. The terminal screw was replaced by a steel cylinder 0.178 inches in diameter that closely matched with the bore of the insulator resulting in a "snug" fit. The center wire was replaced by a nail with the head that also made a "snug" fit in the bore, resting on the shoulder of the insulator, as did the center wire. Both electrode surfaces contacting the resistor mix were dipped in light machine oil, and then in pure copper powder prior to loading and sealing. No copper glass was used.

The standard volume of mix and sealing procedures were used and four spark plugs were sealed using trial resistor mix T4. The average of the resistance values was 1.84 kΩ, the standard deviation was 0.334, and the ratio $\sigma/\overline{X}$ was 0.18. This ratio was the lowest value of any resistor mix in the T, U, or V series, and the average resistance value was also low. These two changes could be due to a significant reduction in the contract resistance because of the larger surface area of the electrodes. These changes could also be due to a significant modification of the conduction path through the resistor material since the flow of the resistor material was limited by the "snug" fit of both electrodes in the bore. A microstructural examination of the sealed resistor material in these plugs showed that the laminar flow was altered. Because of the difficulty in making the customized electrodes, no attempt was made to determine how much of each change (the decrease in the resistance values and the decrease in the scatter of the resistance values) was due to the increased contact area and to the modification in the laminar flow. Both changes were due to the electrode geometry modifications.

APPENDIX D

A CALCULATION FOR THE VOLUME OF TiO_2 IN THE RESISTOR MIX

The following calculation uses geometrical considerations to show that there is enough TiO_2 in the resistor mix to form 25 layers of TiO_2. An average gap distance (the distance from the copper glass to the center wire head) from Table 8 is 37 mm at 50x or, actually, 750 μm. If an average glass layer is 30 μm then there should be 25 glass layers between the copper glass and the center wire head. About 25 glass-TiO_2 layers can be counted in the gap in the photomicrographs in Figures 17 and 18 (note the overlap of these two figures).

Suppose each layer is 3 mm in diameter and 3 μm thick. The volume of 25 layers is calculated to be 5×10^{-4} cm^3. A resistor mix contains 10 w/o TiO_2. The bulk density of the TiO_2 is 0.55 g/cc and 193 mg of resistor mix are in each spark plug. Therefore, there is 3.5×10^{-2} cm^3 of TiO_2 in each spark plug. This value is 70 times more than is needed to form 25 layers of the dimensions used above. These dimensions are intended to be larger than actual layer dimensions. Of course, much of the TiO_2 is in layers next to the insulator walls. This calculation was presented to show that there is enough TiO_2 in the resistor mix to create electrically continuous layers in the resistor mix.

BIBLIOGRAPHY

1. R. A. Webb, K. Schwartzwalder, and P. N. Keston, "Resistor Composition," U. S. Patent 3,567,658, March 2, 1971.

2. M. Oki, et al., "Resistor Built-In Spark Plug," U. S. Patent 4,004,183, January 18, 1977.

3. F. E. Heischman, "Resistor Compositions and Spark Plugs Having Integral Resistors," U. S. Patent 3,088,921, May 7, 1963.

4. R. R. Burgett, R. E. Massolle, and D. R. Van Uum, "Relationship Between Spark Plugs and Engine-Radiated Electromagnetic Interference," IEEE Transactions on Electromagnetic Compatibility, Vol. EMC-16, No. 3, p. 160, August 1974.

5. Anonymous, "Reduced Ignition Interference," Electronics, Vol. 22 (2), p. 118, July 1949.

6. K. Schwartzwalder and A. S. Rulka, "Spark Plug Electrode Seal," U. S. Patent 2,248,415, July 8, 1941; J. E. Blum and J. W. Ezell, "Spark Plug with a Conductive Glass Seal Electrode of Glass, Copper and Zinc," U. S. Patent 3,349,275, October 24, 1967.

7. W. E. Counts, R. W. Smith, and K. Schwartzwalder, "Resistor and Spark Plug Embodying Same," U. S. Patent 2,864,884, December 16, 1958.

8. T. G. McDougal, K. Schwartzwalder, and A. S. Rulka, "Resistor and Spark Plug Embodying Same," U. S. Patent 2.459,282, January 18, 1949.

9. W. E. Counts, R. W. Smith, and K. Schwartzwalder, "Resistor Composition and Devices Embodying Same," U. S. Patent 3,235,655, February 15, 1966.

10. M. Yoshida and M. Sakai, "Self Sealable Glassy Resistor Composition for a Resistor Sealed Spark Plug," U. S. Patent 4,006,106, February 1, 1977.

11. G. Skinner, H. L. Johnston, and C. Beckett, Titanium and Its Compounds, A Review of the Literature, H. L. Johnston Enterprises, Columbus, 1954.

12. A. H. Ioffe, Physics of Semiconductors, Academic Press, New York, 1960, (translated from the Russian).

13. G. V. Samsonov, ed., The Oxide Handbook, IFI/Plenum, New York, 1973, (translated from the Russian).

14. H. K. Henisch, "Thermo-Electric and Conductive Properties of Blue Titanium Dioxide," Electrical Communication, Vol. 25, p. 163, 1948.

15. J. H. Becker and W. R. Hosler, "Multiple-Band Conduction in N-Type Rutile (TiO_2)," Physical Review, Vol. 137, No. 6A, p. A1872, March 15, 1965.

16. M. D. Earle, "The Electrical Conductivity of Titanium Dioxide," Physical Review, Vol. 61, p. 56, 1942.

17. H. H. Hausner, "Semiconducting Ceramic Materials," Journal of the American Ceramic Society, Vol. 30, No. 9, p. 290, 1947.

18. J. Takahashi, I. Yamai, and H. Saito, "Effect of Additives on the Sintering and the Electrical Conductivity of TiO_2," Yogyo-Kyokai-Shi, Vol. 83, No. 12, p. 589, 1975.

18b. R. G. Breckenridge and W. R. Hosler, "Electrical Properties of Titanium Dioxide Semiconductors," Physical Review, Vol. 91, No. 4, p. 793, 1953.

19. Per Kofstad, Nonstoichiometry, Diffusion and Electrical Conductivity of Binary Metal Oxides, p. 137, John Wiley and Sons, Inc., New York, 1972.

20. R. F. Bartholomew and D. R. Frankl, "Electrical Properties of Some Titanium Oxides," Physical Review, Vol. 187, No. 3, p. 828, 1969.

20b. A. L. Avdeev, Y. L. Danilyuk, and L. A. Rozenberg, "Mechanism of Electrical Aging in Titanium Dioxide," Izvestiya Akademll Nauk SSSR, Neorganicheskie Materialy, Vol. 8, No. 2, p. 263, 1972, (translated from the Russian).

21. O. A. Golikova, et. al., "Thermoelectric Properties of Semiconducting Materials with a Nonstandard Conduction Mechanism," Soviet Physics-Semiconductors, Vol. 6, No. 9, p. 1488, 1973.

22. R. R. Ridgway, "Boron Carbide," Transactions of the Electrochemical Society, Vol. 66, p. 117, 1934.

23. T. Sugaya and O. Watanabe, "Electric Conduction of Boron Carbide," Physica Status Solidi (A), Vol. 15, p. K181, 1973.

24. V. S. Neshpor, V. P. Nikitin, and V. V. Rabotnov, "Studying Certain Electrical and Physical Properties of Pyrolytic Boron Carbide," Soviet Powder Metallurgy and Metal Ceramics, No. 11, (71), p. 889, 1968, (translated from the Russian).

25. L. M. Litz and R. A. Mercuri, "Oxidation of Boron Carbide by Air, Water, and Air-Water Mixtures at Elevated Temperatures," Journal of the Electrochemical Society, Vol. 110, No. 8, p. 921, 1963.

26. T. N. Nazarchuk and L. N. Mekanoshina, "The Oxidation of Boron Carbide," Soviet Powder Metallurgy and Metal Ceramics, No. 2 (20), p. 123, 1964, (translated from the Russian).

27. D. A. Dominey, "Reaction of Boron Carbide with Oxygen and the Effect of Preirradiation in a Nuclear Reactor," Chemical Society, London, Journal (A), p. 712, 1968, Part I.

28. G. W. Morey, The Properties of Glass, pp. 477-489. Reinhold Publishing Corporation, New York, 1954.

29. H. J. Van der Westhuitzen, W. C. A. Van Niekerk, and W. J. de Wet, "Glass Resistance Measurements," Journal of the American Ceramic Society, Vol. 58, No. 11-12, 1975.

30. T. P. Dgebuadze and O. V. Mazurin, "Investigation of the Electrical Properties of Low-Alkali Borosilicate Glasses," Inorganic Materials, Vol. 4, Pt. 3, p. 1330, 1968, (translated from the Russian).

31. L. F. Oldfield and R. A. Wright, "The Volatilization of Constituents from Borosilicate Glass at Elevated Temperatures," Glass Technology, Vol. 3, No. 3, p. 59, 1962.

32. P. G. Heslop, "The Properties of Borosilicate Glass," Laboratory Practice, Vol. 17, p. 1024, 1968.

33. C. G. Wilson and A. C. Carter, "The Self-Diffusion of Sodium Ions in a Borosilicate Glass and a Soda-Lime Glass," Physics and Chemistry of Glasses, Vol. 5, No. 4, p. 111, 1964.

34. J. R. Hutchins, III and R. V. Harrington, Glass, reprinted from Kirk-Othmer, Encyclopedia of Chemcial Technology, 2nd ed., Vol. 10, p. 533, John Wiley and Sons, Inc., New York, 1966.

35. Personal Communication with R. Feeney.

36. Personal Communication with B. Finzel.